Physics – Uspekhi **40** (9) 925 – 949 (1997)

REVIEWS OF TOPICAL PROBLEMS PACS numbers: **74.72.–h**, **74.90.+n**

Cuprate superconductivity: some spectroscopic, structural, and chemical aspects

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Contents

Abstract. HTS results obtained by steady-state and time-dependent spectroscopy of spontaneous Raman scattering and by the quantum-beat technique are analyzed. The copper – oxygen chain structure is analyzed by invoking the charge-density-wave concept and the donor – acceptor interaction between chemical-bond partners. Stimulated Raman and hyper-Raman scattering and the low-frequency acoustic spectroscopy of spontaneous Raman scattering are discussed in terms of their prospects for HTS experiments.

1. Introduction

The long history of investigations of conventional ('low-temperature') superconductivity is a matter of common knowledge. A new powerful impetus to the development of this fundamental avenue of investigations in physics and technology was given in 1986 when radically new materials — cuprates — possessing a high-T_c superconductivity (HTS) were discovered [1]. Shortly thereafter, Wu et al. [2] found a compound for which the critical superconducting temperature T_c was well above the liquid-nitrogen temperature [2]. This essentially simplified experiments and offered considerable promise for diverse engineering applications (see, for example, Ref. [3]). By now no less than ten thousand works have been made in the field of HTS. There have been a plethora of conferences, symposia and workshops, a number of new periodical editions were established, and a great many reviews and monographs on selected problems were written. All this may be compared with the boom in nonlinear optics in the 1960s – 1970s.

In the context of problems of HTS, a wide variety of well-known technical tools and methods for the study of substance have been used. Among these, Raman scattering (RS) spectroscopy in its spontaneous resonance version has occupied one of the top place. This review is devoted to selected problems of this line of investigation. The author restricts his consideration to scattering by phonons, and the experimental data obtained by other physical methods are only invoked to the extent that is necessary for solving the main problem. In addition, the principle of analyzing spectroscopic data in correlation with the structural and chemical peculiarities of cuprates and their conjectural interpretation is consistently implemented.

It is no wonder that the traditional method of spontaneous RS is still widely used up to now in the physics of HTS. Indeed, it allows the needed information about phonon states in a system to be obtained. It is, however, strange that other mechanisms and variations of the process of RS, such as coherent, stimulated, and three-phonon (rather than the usual two-phonon) scattering, proved to be beyond the view of scientists in spite of the fact that they provide new scientific information. One of the goals of this review is to demonstrate this fact with several examples.

The review is constructed in the following manner. In Section 2, the specific features of the structure of cuprates and the character of potentials acting between some ions are briefly discussed. The role of the anharmonicity of vibrations is specially emphasized. The physical principles of the vibronic theory of RS are given as well as those of the

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Received 23 July 1996, revised 24 April 1997
Uspekhi Fizicheskikh Nauk **167** (9) 973 – 999 (1997)
Translated by V M Matveev; edited by S N Gorin

quantum-beat method which, despite its 'youth', has already found application in studies of cuprates.

Section 3 provides information on the details of RS experiments. In this section, particular emphasis is given to the advisability of applying charge-coupled devices for the detection of radiation scattered by cuprates.

In Section 4 (the largest by volume), a number of peculiar features of the phonon mechanism of HTS is considered. The concept of the donor–acceptor interaction which was proposed and qualitatively substantiated for cuprates with a copper-oxygen chain subsystem holds a central position in this section. This enables 'a bridge' to be built between the results for cuprates and quasi-one-dimensional semiconducting and conducting systems and, thus, to introduce in the description of the process of HTS the concept of collective modes in RS spectra. The advantage of such an approach is the natural way of interpreting the strong electron – photon interaction inherent in cuprates. This fact forms the basis of various models of HTS. Furthermore, in this section the author goes into the problems of domain structures of cuprates, high-frequency RS bands, the anharmonicity of vibration modes, the nonadiabaticity of states, and others. The latter property is intimately connected with a number of peculiarities of cuprates revealing themselves when isotopic substitution of oxygen is used.

In the literature particular attention is given to the study of the processes of distribution and motion of oxygen vacancies and their interaction with the crystal lattice. The main contribution to solving this problem was made through the use of a non-traditional techniques based on time-domain RS spectroscopy. These techniques and the associated results are discussed in Section 5. Here, in author's opinion, of most interest is the effect of photogeneration of forbidden vibration modes which is observed in combined studies of the RS and IR absorption spectra of cuprates.

Although the quantum-beat method is as yet 'young' and its application to the problems of HTS is described in only two publications, the author believes that it makes sense to present the obtained results in Section 6. The reason is that this method provides fundamentally new scientific information concerning, for example, the temporal change of electron–phonon interaction, which is of prime importance for the overall physics of HTS, and phonon spectroscopy in particular.

Finally, in Section 7, a prognosis is made on the prospects and ways of using new RS spectroscopy techniques in studies of HTS. The low-frequency acoustic region of RS, two variations of stimulated RS, and hyper-Raman scattering are discussed.

2. Initial premises for the investigation of superconducting cuprates

A considerable advance in the understanding of the physical essence of superconductivity in metals came about through the well-known classical work by Bardeen, Cooper and Schrieffer (BCS) [4]. Undoubtedly, of fundamental importance was the fact that these authors introduced the key concept of Cooper pairs in the physics of superconductivity. The Cooper pairs are formed by excited electrons with antiparallel spins and are the major charge carriers, whose energy is less than the normal state energy and proportional to the quantity $(\hbar\omega)^2$, where ω is the lattice vibration frequency (the latter provides an explanation for the isotopic effect). Subsequently, this concept was generalized and extended to the case of paired holes. Nowadays the hole mechanism of HTS is commonly accepted.

The BCS theory developed within the approximation of a weak electron – phonon interaction (EPI) was based on experimental data available at that time and, in particular, on the results of measurements of T_c for mercury isotopes [5, 6]. These measurements allowed the establishment of the important quantitative relationship $\delta T_c/T_c = -\alpha\delta M/M$ between the relative change of T_c and the mass M of vibrating nuclei. It turned out that $\alpha = 0.5$. On the other hand, according to the BCS theory [4], the critical transition temperature can be written in the form $T_c = 1.13\theta_D \exp(-1/\lambda)$, where λ is the EPI constant (only slightly depending on M) and θ_D is the Debye temperature.

At first, the tempting idea of extending the BCS theory to the description of HTS in cuprates arose. However, the assumption of a weak EPI in the cuprate-type compounds immediately seemed doubtful and collapsed when tested by many direct and indirect experiments. Moreover, several mechanisms were suggested which might be responsible for considerable EPIs. Because of this, one was forced to resort to the modernized BCS theory [7, 8] as well as to take into account the anharmonic properties of real vibration modes in the form of concrete dynamical models. In this regard a series of papers coming from Bogolyubov's school of thought are worthy of attention (see, for example, Ref. [9]).

In connection with the problem of revealing the nature of HTS, experiments on the isotopic effect when replacing some ^{16}O oxygen ions by the ^{18}O ions were of great importance. The early works of this line of investigation showed the total absence of this effect. Only in the most recent experiments was the situation demonstrated to be different. As an example we refer to the authors of Refs [10 – 14] who report that for cuprates differing in composition this isotopic substitution of oxygen can result in a considerable change of α going even beyond the limits predicted by the BCS theory. It was also found that the effect is acutely sensitive to the technology of enriching samples in the relevant oxygen isotope (depends on which types of crystallographic sites are occupied by this isotope). The increased anharmonicity of vibration modes and the non-adiabaticity of states leave their imprint on the results of measurements, so that it is difficult to separate the contributions from α and λ to the isotopic effect.

Thus, a rather difficult situation arises. It may be further complicated by the tendency of some cuprates to form clusters. Therefore, extreme care should be exercised when inferring a true mechanism of HTS from the data on the isotopic effect and a closer look at side effects is called for.

In the physics of superconductivity the concept of double-well potentials proved fruitful. These potentials, as applied to cuprates, describe the movement of apical (bridge) oxygen atoms [15], which was confirmed by observing near-edge X-ray absorption fine structure [16]. This fact allowed an understanding of the nature of a rather large anharmonicity inherent in the vibrations of such oxygen atoms and laid the groundwork for various phonon models of HTS.

The origin of the double-well potentials could be related to the existence of structural instabilities in a system. This was mentioned in literature as a pure empirical fact long before the discovery of HTS. For cuprates having, say, the composition $YBa_2Cu_3O_{7-x}$, the case in point is the transition from a tetragonal phase to an orthorhombic phase for x values at which the superconducting properties of crystals are formed.

Static [17] and dynamic [18] approaches were proposed for describing the process of initiation of such instabilities. What they have in common is taking into account copiously existing structural point defects at which a new phase becomes localized. The dynamic approach also takes into consideration the local-state fluctuations and their mutual relations through anharmonicity. It is believed that the 'guest' and 'host' phases are separated by a low potential barrier which may be overcome at the expense of the energy of electrons and phonons. The corresponding processes are known as 'local structural excitations' (LSE). Finally, it is assumed that in superconducting materials a sufficient number of LSE always exist to ensure a change-over from one phase to the other and, thus, to realize a structural instability.

It is significant that some local states may also reveal themselves on the macroscopic level in the sample volume, which determines many properties of a material such as its elastic properties, the occurrence of stresses, and so on [19]. Therefore, both of these theories do not preclude the possibility of 'freezing' one or another phase, that is, its transformation to a metastable state, especially at low temperatures, as well as creating small-scale clusters. The latter fact was used by Phillips [20] in his consideration of the isotopic effect in cuprates. It is the author's opinion that in connection with this fact there is no need to invoke exotic 'phonon-free' models of HTS.

As is known, cuprates belong to a wide class of compounds that are referred to as 'layered' since they are formed from 'sandwiches' involving various elements. Such compounds can crystallize in the form of so-called polytypes, which have nearly the same structure and energy and whose structures only differ in the relative displacement of layers. This strongly affects the physical properties of these compounds and is favorable to the formation of not only double-well, but also multi-well potentials.

From the standpoint of spectroscopy and HTS physics as a whole, the situation when the double-well potential arises as a result of removing the degeneracy of high-symmetry states through the dynamical Jahn–Teller effect is of great importance. This situation is essentially related to the giant EPI and concerned with the most important aspects of HTS, such as the pairing mechanism and others. It was the subject of a large body of research, both experimental and theoretical. A brief summary of the results and a bibliography on this problem can be found in Ref. [21].

Considering the problem of vibration anharmonicity, the author concentrates his attention on a special case, namely, on a special form of the operating potential. However, anharmonicity is inherent in any system to some degree. In solids, it is the anharmonicity that determines the frequency shift of vibration spectral lines and bands, for example, in RS spectra under the action of a pressure applied to a sample. Experiment and theory show that the effect of anharmonicity is most pronounced for surface atoms and ions. The smaller the dimensions of particles (on a scale of 1 – 10 nm), the more pronounced the effect. The dimensional dependence of T_c in the particles of various metals was studied time and again including a consideration of the anharmonicity of vibrational degrees of freedom [22].

For the present, the case in point was the natural anharmonicity, a primordial property of substance. However, under certain conditions the anharmonicity may be induced by an intense electromagnetic field. This is the situation of stimulated RS (SRS): the pulses of light induce vibrations so large in amplitude that their anharmonicity cannot be ignored [23]. Also of great importance is the spatial and temporal coherence of these vibrations, which suggests a more or less sharp increase in carrier concentration during the generation of the SRS process [24].

Thus, considering the natural and induced anharmonicity of vibration modes is one of the important starting points of research, in particular from the viewpoint of the application of spectroscopic methods. Therefore, it is appropriate to briefly summarize the fundamentals of the process of RS before the main text.

Over the last three decades, a modification of the quantum theory of RS supposed in Ref. [25] and worked out in detail in Ref. [26] received general acceptance. The essence of this version is that it combines two different approaches, namely, the consistent consideration of the vibronic structure of the scattering-active absorption band, that is, the Franck–Condon interaction on the one hand, and the concepts of the vibronic spectroscopy concerning the mixing of different electron states through the non-fully symmetric vibration coordinates, on the other hand.

Here, the total eigenfunction is written in the adiabatic approximation. The coefficient of the Herzberg–Teller interaction h_a is directly introduced into the expression for the matrix element of polarizability. As a result of all operations, this expression falls into three terms: A, B and C (according to [25, 26]) which depend differently on the frequency of exciting light.

Of real interest are the terms A and B. They describe the intensity of all fully symmetric vibrations and those of non-fully symmetric vibrations that are active in mixing, respectively. Selective enhancement of the first type of vibrations takes place at resonance with a strong allowed absorption band, and of the second type, when excitation is accomplished within a weak allowed component of a forbidden band and this component 'steals' its intensity from the strong band of a vibration-related electron transition. The term A may be responsible for the multiphonon scattering observed in the form of a series of various higher harmonics and combination tones. The contribution of the term C to scattering is small since it takes into account the vibronic interaction of normal and excited electron states, which may take place in very rare cases. Therefore, in the framework of the outlined theory some vibration modes drop out of consideration.

There are some other difficulties in the use of this theory. However, they are not of a fundamental nature. These are the limited nature of the adiabatic approximation and the need to take into account the interaction of different vibration coordinates, which is of prime importance for cuprates because this interaction is effected through anharmonicity.

Another characteristic feature of the vibronic approach to the process of RS is that, strictly speaking, this is only applicable to simple systems formed by molecules or small-size particles. In the case of extensive systems, such as polymers or crystals, the fully symmetric vibrations with their well-developed higher-order scattering structure do not contribute to the RS spectra. Indeed, the term A which is responsible for these vibrations vanishes since in this case the excitation is 'spread' all over the system and the position and form of the potential surfaces of the normal and excited states remain unchanged.

However, a great many experimental results are in contradiction with this conclusion. For example, in the

resonant RS spectrum of the CdS single-crystal nine higher harmonics of one of the vibration modes were found [27]. According to Cardona, such a paradox is caused by the presence of localized states in the crystal [28]. They are highly probable in the case of cuprates. In the subsequent discussion, it will be shown that this is indeed the case.

As was mentioned above, many cuprates have an inhomogeneous structure. This implies a reduction of their period of identity, which results in the violation of the law of conservation of momentum, which rigorously holds only for rather large crystals of high quality. As a consequence, in the case of cuprates the ban on vibrations with $\mathbf{k} \neq 0$, where $\mathbf{k}$ is the wave vector of phonons, must be removed. This may result in a one-sided broadening of some spectral lines. Such an effect was observed time and again and given an adequate, even if ambiguous, interpretation [29 – 31].

On summing up all outlined above, it may be concluded that the theory put forward by Albrecht et al. [25, 26] is, even in its original form, an appropriate instrument for the study of HTS, allowing one to judge the selection rules and intensities of vibrational transitions and, hence, obtain unique information on the structure and morphology of corresponding materials. Of importance is the fact that RS spectroscopy in its resonant version simultaneously reflects the characteristic features of both normal and excited electron states of systems.

Now, we consider in an extremely brief way the principle of the quantum-beat method. In its original version two pumping light beams formed by single pulses of the same laser were sent to a sample (liquid or solid — crystal, glass) at an angle to each other. The pulse width τ was subject to the condition $\tau < 2\pi/\omega$, where ω was the frequency of a chosen optical mode. Depending on the concrete value of τ, a wide frequency range is covered, from the lowest frequencies of the order of small fractions of inverse centimeters to several hundred inverse centimeters typical of vibration transitions. It is obvious that the upper limit of accessible frequencies is completely determined by the possibilities for producing ultranarrow pulses, that is, by purely technical factors (the availability of an appropriate laser).

Under the action of pumping, coherent elastic standing waves are excited in a sample. Their coherence is achieved owing to the overlap of different states by broadened ultrashort pulses. These states may interfere, which manifests itself in a series of peaks during time-base sweep of spectra, the so-called quantum beats (with an appropriate period). The system is interrogated by a probe pulse of the same duration from the same laser, but with a time delay. Since the latter can be varied within a period of pumping pulses, it is possible to obtain signals for different phases of elastic waves induced in a sample. Hence, arose the name 'intrapulse' stimulated Raman spectroscopy for this technique (we especially stress the first word).

Quantum beats can also be excited in the single-beam mode. In principle, such an experimental scheme is even preferable. In this case, however, one deals with the excitation of progressive elastic waves. The subjects under consideration are detailed in review [23].

Thus, when light pulses induce standing or progressive waves (depending on concrete experiment) in the medium, they are scattered by these waves, which is, with reservations, analogous to the process of self-focusing, that is, in both cases self-action of radiation via the scattering medium takes place.

The complex physics of quantum beats in transparent materials becomes even more complicated if the pumping is accomplished within their absorption bands, that is, under resonance conditions. In this situation the cross section of RS enters into a complex expression, which affects the corresponding selection rules [23]. This is a fact of great importance, particularly for investigations of cuprates by this method. Experimentalists have already encountered this phenomenon. Although the theory of this question has already been considered in several publications, it may not be considered for the present as a full-blown theory. The problem of selection rules still remains 'off screen' and needs further development.

Thus, owing to its capabilities, RS spectroscopy taken in a broad sense has already become one of the most important optical methods used for studying HTS. Although there have been published many reviewing papers on this subject, it is not unreasonable to consider once again the results already obtained taking into account the recent advances in experimental techniques which make it possible to perform unique measurements of kinetic parameters. The author is certainly aware that the choice of questions taken up in this review is to a large degree subjective and is determined by the partialities of its compiler. A number of reviews lively in form and fundamental in content, and, in addition, covering a broad spectrum of superconductivity problems have been written by Ginzburg and followers of his school of thought. Therefore it is pertinent to refer to their last reviews [32 – 34].

3. Experimental details

It is known that the spontaneous Raman spectra of cuprates and related materials are very weak. This is first of all determined by very high absorption of light. For example, even in the dielectric phase of the $YBa_2Cu_3O_6$ cuprate the extinction coefficient is on the order of 10^5 cm^{-1} [35, 36]. For this reason the penetration depth for exciting light is very small. Its value is usually about 150 nm. Besides, all spectra are characterized by the presence of a continuous background of physical and instrumental origin most pronounced in the vicinity of an exciting line. Because of this, experiments can be conducted successfully only using double or even triple monochromatization of light, high-sensitivity detectors, and other modern tools for the registration of spectra.

As for two last questions, new multichannel light detectors, the so-called charge-coupled devices (CCDs), holding the greatest promise for optics and spectroscopy, are beginning to become the routine practice in studies of cuprates. These detectors are based on multielement semiconductor structures in which charge is the measured quantity [23].

Among the exceptionally valuable technical characteristics of CCDs are the practically total absence of noise, a high quantum yield with a maximum in the vicinity of 600 nm, and a wide dynamic range. All this provides the basis for the application of CCDs in Raman spectroscopy under red excitation, when a substance strongly absorbs more short-wavelength radiation and exhibits intense luminescence. Cuprates fall into just such a category.

Decisive advantages of CCDs enables one to reduce a power level for exciting RS to a value below 3 mW [37, 38], which is of great importance. This results in decreasing the side action of incident radiation on the objects under investigation manifested in heating the samples and the induction of charge carriers in them. The latter effect is best

to induce using an independent source providing the separation of both functions of incident radiation.

Another possibility to increase the sensitivity of the measuring apparatus as a whole is using the traditional detectors, namely, photomultipliers or optical multichannel analyzers in combination with image amplifiers on the basis of microchannel plates. Here, it is important to keep in mind that in the last case, experiments may be realized in a number of ways, for example, using several multichannel plates, which ensures high and stable amplification.

Unique high-sensitivity experimental equipment on the basis of multichannel analyzers and multichannel plates was developed by Goncharov et al. [39] and applied, in particular, to studies of HTS. Most of other authors used standard apparatus for this purpose, modernized in some way or another (see, for example, Ref. [40]).

It should be, however, borne in mind that for all the variations of experimental equipment, the case in point is the registration of spectral lines in the absence of a background. At the same time, in the case of cuprates the phonon RS spectra are superimposed on a background resulting from Raman scattering by electrons and luminescence. This background will impose a limitation on the threshold sensitivity for measurements of the line portions of RS spectra.

There exists, however, a tested method to obtain phonon RS spectra of cuprates free from the unfavorable effect of such a background. It consists in exciting spectra in the region of transparency of cuprates with the use of a continuously operated YAG : Nd laser with a wavelength of 1.06 μm and a Fourier-transform spectrometer as the optical apparatus [41]. True, all advantages of resonant RS, such as gaining total information on the actual transitions in electron absorption and some others, are lost.

The above-mentioned source of exciting RS in cuprates produces the greatest wavelength of incident radiation. In the short-wave spectral region the extreme position is held by the excimer pulsed XeCl laser (308 nm) used recently in time-resolved experiments on HTS [42]. In addition, continuously operated ultraviolet lasers with wavelengths of 325.0, 334.5, 351.1 and 364.8 have been used for investigations [38]. In these lasers, a mixture of He–Cd and Ar^+ is used as a working medium. Needless to say that the great majority of results were obtained when RS was excited in the visible range using lines of the argon, krypton or Ar + Kr lasers.

From the experimental standpoint, of importance is the fact that the RS method needs for probing rather small amounts of substance and, in addition, small surface areas of samples. The latter is accomplished by the use of microlenses [43]. An application of such a technique allows one to isolate light spots with diameters of about 1 μm, which is of fundamental importance in certain situations.

Ceramics, single crystals, and rather thin crystalline films may serve as the objects of investigation using RS spectra. Experiments with ceramics are usually undertaken to obtain preliminary data, identify the side phases of synthesis hindering the interpretation of spectra, and in cases where certain technological difficulties in the preparation of single crystals emerge. At the same time, investigations of oriented single crystals and, partly, films give fundamental information that is necessary for assignment of the spectra observed to the structure of the corresponding scattering centers and the symmetry of vibrations. In addition, films are of interest from the viewpoint of their application in various devices.

It is the author's opinion that, in connection with the preceding, the application of iodine filters placed in front of the entrance slit of a monochromator for depressing the excited line (514.5 nm) of an argon laser deserves much attention, especially for investigation of ceramics [44]. This is of great interest in the case where the object of investigation is the low-frequency acoustic region of the RS spectra characterizing the submicroscopic structure of samples, since for cuprates such a problem is difficult to solve using the traditional method of grazing-incidence X-ray scattering.

It is a matter of common knowledge that in the resonant RS spectroscopy of various objects of great importance is the construction of the excitation profiles, that is, the dependences of the electrooptical characteristics of spectra on the frequency of incident radiation. Clearly, this technique was also found practical use in studies of HTS. Moreover, it was extended to the absolute cross sections of the RS process [35,36].

The cross-section measurements were conducted, in particular, for cuprates of composition $YBa_2Cu_3O_7$. Comparable data were obtained by way of recalculation with the formula

$$S_{is}(\omega) = \frac{v}{(4\pi)^2}\left[\frac{\omega}{c}\right]^4 \left|\frac{\mathrm{d}\varepsilon_{is}(\omega)}{\mathrm{d}Q}\right|^2, \tag{3.1}$$

where i and s are the polarization directions for the incident and scattered light, respectively; ω, v, and c are the exciting frequency, the unit-cell volume, and the velocity of light, respectively; ε_{is} is the complex dielectric tensor; and Q is the normal coordinate. The amplitude of the vibrational displacement of the nth atom was written as $Qe_n(\hbar/2M_n\omega_{\mathrm{ph}})^{1/2}$, where e_n and ω_{ph} are the eigenvectors of the phonon and its frequency, respectively. Independent data on absorption, reflection, and refraction were taken into account†.

Turning now to quantum-beat spectroscopy, we should recall that its realization is possible in two ways: with one-beam pumping or with pumping with two beams directed onto a sample at fixed angles. To enhance the effect in both cases more or less long trains of pulses correlated in phase are used rather than single pulses. The pulse-train technique was also applied to investigate this effect in some opaque materials including cuprates [45–47].

The objects of investigation [45] were crystals of bismuth and antimony. Quantum beats were excited using the one-beam technique. A Q-spoiled laser producing in-phase-correlated pulses was used. The pulse width was about 78 fs, its energy 1.98 eV, the repetition rate 100 MHz. The average power did not exceed 5 mW, which practically eliminated a thermal effect. In a more recent paper by other authors, it was shown that under similar conditions the temperature rise was no more than 2 K. To avoid the effect of pumping on the probing radiation and, eventually, on the measured signal, both the exciting and probing beams were polarized in mutually perpendicular directions. The pumping-radiation wavelength was 630 nm. The output signal represented the relative change of reflectivity of the film. The spectral device was based on the Fourier transform.

A similar technique was used in the first work on quantum beats in a dielectric film of cuprate [46]. However, in this case the modulated relative transmission of the film was measured

† Here and below the designations used in the original papers will be retained in all formulas.

with the use of an original mixing technique described in Ref. [48]. The authors reported that the threshold sensitivity of their experimental set was 10^{-5}.

An important advancement of the experiment, which extended its capabilities, was using an optimized method of measuring ultranarrow pulses [47]. Owing to this method, the threshold sensitivity of the apparatus for measuring the reflected signal was brought to about 10^{-7}, which made it possible to obtain results of fundamental importance [47].

In connection with studies of the dynamics of carriers, that is, the transport features of HTS, in some cuprates and some other problems, the well-established methods of time-resolved RS spectroscopy covering the range from milli- to femtoseconds and, in particular, using the controlled time delay of an interrogating pulse have found wide use. In such experiments not only RS spectra, but also luminescence and transmission (absorption) spectra are detected. Methodically, it is of interest that in the latter case CCDs are used in experimental setup.

On the basis of experiments in which RS spectra were detected [49], important information on the motion and ordering of vacancies in the bulk and on the surface of samples was obtained. In this work, pumping and interrogation of the system by millisecond pulses was used. The authors succeeded in observing the formation of an extra density of carriers generated in the system upon irradiation with pulsed and continuous-wave nitrogen lasers (time range of about 0.6 ns).

Thus, it may be concluded that there exist a variety of technical tools already used in studies of HTS by different RS spectroscopy methods. Nevertheless, there is still much room for further improvements in this field. The author believes that it is advisable to devote a separate section of this review to this subject.

4. Phonon mechanism of the process of HTS

4.1 Insight into the structure of cuprates

It has already been mentioned that cuprates belong to an important and wide class of layered compounds. In most cases their structures are well-determined with the use of diffraction techniques and electron microscopy†. Following is a brief description of the unit cells of the cuprates that are discussed in this review.

The crystals of composition $YBa_2Cu_3O_{7-x}$ (in the following designated for brevity as 1:2:3) are the best-studied compounds. They exist for all values of the stoichiometric index x in the range from 0 to 1. The upper limit (1) of x corresponds to a tetragonal (nonconducting) phase, the low one (0), to an orthorhombic (superconducting) phase. Their unit cells along with the designation of the axes are shown in Fig. 1 and Fig. 2.

Note that in both phases the copper atoms occupy two inequivalent crystallographic sites — Cu(1) and Cu(2). For oxygen atoms, five nonequivalent positions exist in the superconducting phase. The probability of occupation of oxygen sites in the basal plane is determined by the oxygen stoichiometric index. The Cu(2), O(2) and O(3) atoms form layers of quadrangular vertex-shared pyramids with a copper

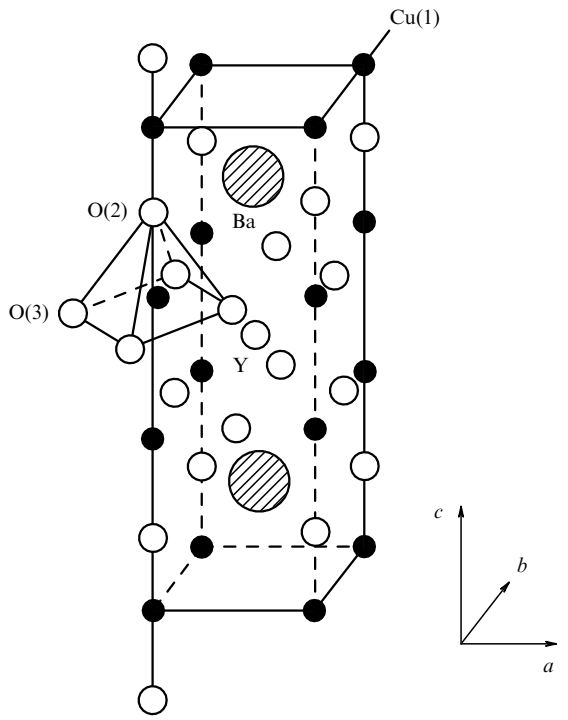

Figure 1. Unit cell of the dielectric phase of the 1:2:3 crystals [51].

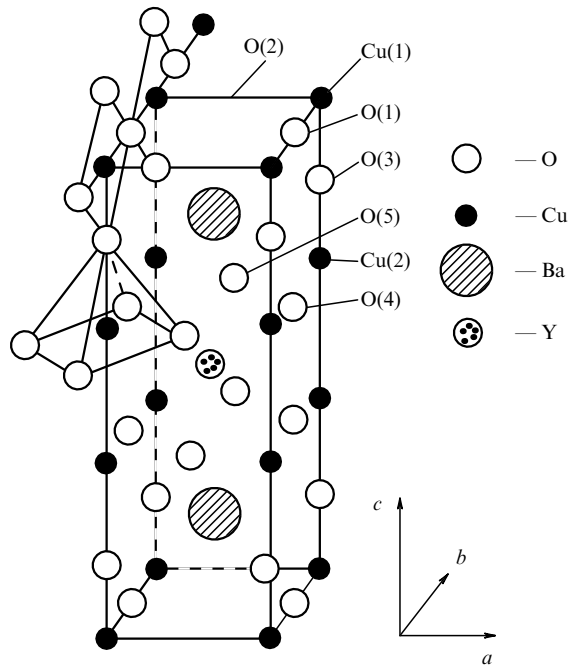

Figure 2. Unit cell of the superconducting phase of the 1:2:3 crystals [51].

atoms lying virtually at the centers of their bases. These layers are bound together by the apical (bridge) oxygen atoms O(4) playing an important, if not pivotal, role in the process of HTS for the 1:2:3 type materials. It is believed that 2O(1), O(4), and Cu(1) atoms form tapes from which line chains can be singled out. In the following this question will be given special emphasis. Furthermore, the unit cells of both phases contain three blocks with barium and yttrium atoms in the center. In our consideration these structures are of secondary importance. Depletion of the orthorhombic phase of oxygen leads to the progressive breaking of layer-to-layer bonds via

† For now, by 'structure' is meant the spatial arrangement of nuclei and the internuclear spacings. In a wider sense, this concept also involves the nature of resulting bonds (see below).

oxygen O(4) and their disappearance in the tetragonal phase [51].

It is significant that depending on the technological history of samples and the value of x, various structural situations can be realized, and, in particular, a new superconducting phase arises at temperatures of 60–40 K. This was the subject of much investigation using RS spectroscopy. Although this question is of great importance, in the subsequent text it will be touched casually, since it does not bear a direct relationship to the subject matter of the review.

It is believed that pure La_2CuO_4 crystals do not exhibit superconducting properties. They becomes superconductive at temperatures 30–40 K only after doping with Ba and Sr ions having a valence other than La. Structurally (Fig. 3), these crystals are composed of near-plane layers of strongly deformed octahedrons with copper–oxygen bonds, alternating with lamellar structures of composition $La_{1.8}A_{0.2}O_2$, where A = Ba, Sr [52].

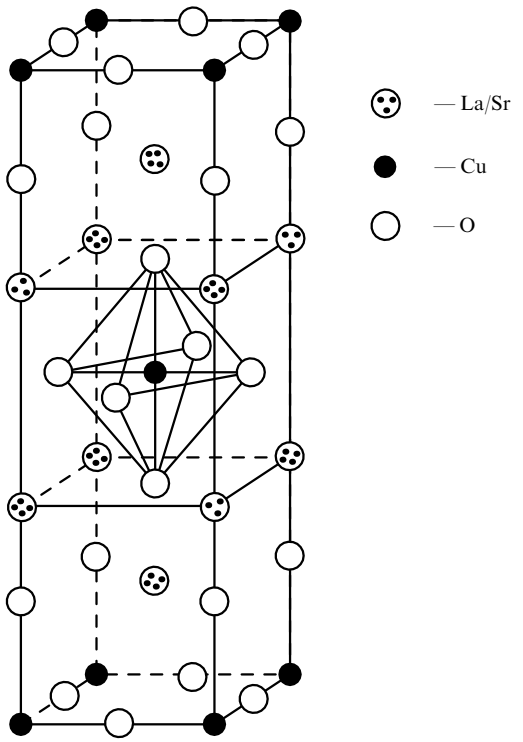

Figure 3. Unit cell of a doped crystal of La_2CuO_4 [52].

In the context of the problem of high-frequency RS bands, which we will touch on below, an interesting cuprate-type compound, $Ca_{1.8}Sr_{0.2}CuO_3$, having a copper-oxygen purely chain structure was synthesized. In the framework of the usual concepts, these chains are correlated with squares formed from the O(1) and O(2) ions with copper atoms in the centers. This can be seen in Fig. 4, where the unit cell of the initial model crystal of Ca_2CuO_3 is presented [53].

Thus, even a cursory examination of the structures of several cuprates allows the conclusion that they are rather complex systems from the dynamic standpoint. Therefore, a trustworthy interpretation of their vibration spectra requires much preliminary theoretical work. This has been carried out synchronously with experiments since the moment of discovery of HTS. This problem was recently examined in a review of Kitaev et al. [54] from a unified point of view for a

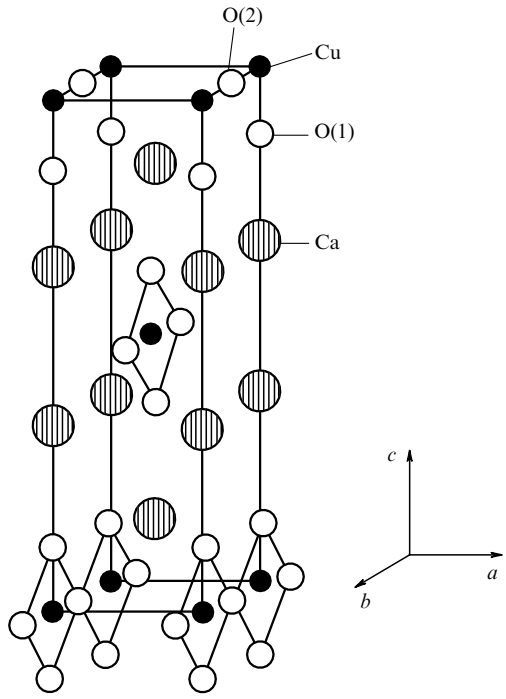

Figure 4. Unit cell of a model crystal of Ca_2CuO_3 [53].

number of compounds of this type including, naturally, the 1:2:3 crystals†.

4.2 Structural and chemical approach to HTS

We focus our attention on the copper-oxygen subsystem of cuprates. First, it should be noted that in a great many works these compounds were considered to be ionic (see, for example, [55–57]). In fact, only in papers [58, 59] was doubt thrown on this point of view and arguments put forward in favor of the hypothesis that certain bonds in cuprates are partially covalent. This hypothesis is supported by data on the bond lengths, which disagree with the sum of corresponding ionic radii and by some other facts and reasoning. It is concluded [59] that the valent Cu–O configuration is formed mainly by hybridization of 3d, 4s and, to a lesser degree, 4p electrons of copper, on the one hand, and 2p electrons of oxygen, on the other. The low-lying 2s states of oxygen are not taken into consideration.

Let us take up the question of the nature of covalent contribution to the Cu–O bonds in the context of donor–acceptor interaction (DAI) [60, 61]. For a purely qualitative analysis of the problem we will use the localized-pair method. First, we will consider crystalline compounds of titanium with oxygen well studied by various methods, including RS spectroscopy, and then turn to a discussion of the situation with cuprates.

The concept of DAI based on the assumption that under certain conditions not only unpaired electrons of two partners, but also donated electrons of a lone pair of one of the partners (oxygen, in our case) take part in chemical bonding. In the process, the second partner must have unoccupied orbitals. The element that in full measure meets this requirement is titanium. It has three vacant orbitals in its

† The author would like to thank M Limonov for giving a chance to read the manuscript of this review well in advance of its publication.

d shell and, according to Syrkin's figurative expression, is one of the most 'holey' elements. Needless to say that the energy expended for the virtual dispairing of the lone pair must be more than compensated by the stabilization of a system at the expense of making new bonds and configurations [60, 61].

The basis for this model is a fundamental principle stated by Syrkin as a result of analysis of many and varied experimental data. According to this principle, there is a well-marked tendency for chemical bonds to be made using not only the usual 'classical' valences, but also additional valences, say, of the DAI type. This is dictated by the requirement of minimizing the free energy of any system.

This interaction affects many microscopic and macroscopic properties of materials. Among such microscopic properties are the elasticity and rigidity of the resulting chemical bonds and the coordination numbers (CN) of atoms, so that the presence of this interaction is adequately reflected in RS spectra. A fundamentally important feature of such bonding is also a tendency to the equalization of electron density at the nuclei of interacting atoms. Because of this, the bonding becomes more or less covalent, which generally results in an enhancement of RS bands. As applied to titanates, all these questions are elucidated in the literature (see, for example, Ref. [62]).

There are a great many facts well compatible with this model. For example, the model provides an explanation for the tendency of the ethers of the titanium acid to polymerization with increasing CN of titanium [61], and the effect of shifting the vibration-mode edge to higher vibration frequencies when passing from compounds with octahedral titanium coordination (with oxygen atoms) to those with tetrahedral coordination, and some other effects [62]. Theoretical calculations have also shown that titanates may be stable only if short-range forces, that is, the covalency of the Ti – O bonds, are taken into account. This is borne out by measurements of the effective charge at titanium nuclei, which is markedly smaller than the nominal charge [63]. It should, in conclusion, be emphasized that titanates are characterized by a very large scattering cross section, which made it possible to perform systematic investigations of crystallizing materials with titanium as an activator.

There is an indirect argument in support of the covalent character of the Ti – O bonds. This is the Pauling's idea of the ways of joining polyhedrons in crystals, namely, at their corners, edges, or faces, as a criterion for the character of bonding. According to Pauling, the covalence increases in this sequence; otherwise, like ions would come closer together and, hence, the repulsive forces would grow. But titanates are the very materials in which polyhedrons join at their edges rather than at vertices.

On summing up the preceding, it may be concluded that the concept of DAI not only gives an explanation for a great many well-known facts, but also allows one to predict a number of new effects concerned with both the mechanics and electrooptics of vibrations in solids which may be tested experimentally.

A considerably more intricate situation arises in cuprates. This stems from the fact that the d shell of a normal copper atom is fully occupied and at the same time cuprates are characterized by a wide variety of valent and coordination forms and configurations.

The normal copper atom has a single unpaired s electron. However, because of the internal regrouping of electrons, $3(d^9sp)$ and $5(d^8sp^2)$ states are excited in copper (here the figures in front of the brackets indicate the number of unpaired electrons). Such a situation is common for all transition-group elements and results from a small difference in energy between the 3d, 4s and 4p shells. If the singly and doubly ionized states of copper are taken into account, the $0(d^{10})$, $2(d^9s)$, $4(d^8sp)$ and $1(d^9)$, $3(d^8s)$, $5(d^7sp)$ configurations arise, respectively.

Thus, it is hard to decide between several possible alternatives without invoking independent data on the real ionization state of copper and its fluctuations in different structural parts of cuprates.

As to information on the degree of the local ionization of copper in 1 : 2 : 3 compounds, this was the subject of investigation using X-ray spectrometry [66]. It was shown that the number of singly charged copper ions in chains is systematically increased with depleting crystals of oxygen. Even more common inferences on this problem were made in Ref. [67] by analyzing a substantial body of literature on high-energy spectroscopy of cuprates and model substances. It turns out that in layers of both dielectric and superconducting phases copper is in a doubly ionized state, whereas in superconducting-phase chains it is in a singly ionized state. These results will be taken below as the starting point for the general consideration of the nature and specific features of Cu – O bonds in chain structures, their adequate manifestations in RS spectra and, above all, their fundamental role in the process of HTS. The above-mentioned results are consistent with the fact that even neutral copper atoms have a rather large value (23 kcal) of electron affinity [65].

In the DAI model, the reduction of the charge at copper nuclei can naturally be related to the large efficiency of the mechanism of dispairing of electrons of the lone pair of oxygen and its competition with the tendency for copper to be ionized. One of the dispaired electrons may be accepted by a p orbital of the copper atom. The additional unpaired electrons themselves go entirely to the strengthening of bonds rather than increasing the CN. This is bound to result in increasing the frequency of the corresponding modes. In any case, one would expect the simultaneous enhancement of the spectra.

The idea of increasing the bond order of separate bonds in chains seems to be fruitful and efficient. Indeed, if so, it would appear natural that chain vibrations are quasicharacteristic. As applied to 'tapes', this assumption implies the presence in them of a preferred direction and, eventually, an apparent decrease in the real CN. From this point of view, copper in chains with squares formed by oxygen atoms has a CN equal to 2 rather than 4.

Taking into account all the preceding concerned with the nature of copper – oxygen bonds, it is rightful to set the question: what is the source of energy expended for dispairing of the lone-pair electrons in oxygen atoms and compensation of electrostatic-interaction forces, that is, for processes determining the realizability of DAI itself. In the author's opinion, much attention should be given here to the assumption that the chains discussed constitute a system of conjugated copper – oxygen bonds. In accordance with the well-known model of a potential well, this structure must be stabilized as a whole to a more or less degree. The longer the chains, the more stable the system [68]. It follows directly that there exists a critical length of segments below which the energy gain is too small and cannot compensate the above-mentioned consumptions of energy. In this case DAI does not

arise and the conventional explanation of the structure of these segments is valid.

In this connection, it is reasonable to consider the results obtained by Uimin et al. [69] concerned an investigation of the dependence of T_c in 1:2:3 cuprates on the nature of oxygen vacancies and the thermal history of samples. Using a thermodynamic approach, the authors conclude that the process of charge transfer into layers proceeds exclusively owing to the segments whose length is no less than four links. For moderate temperatures of quenching and values of the stoichiometric index x of about 0.5, domains form in which most segments have a rather large length and therefore are active in creation of holes in layers.

Thus, the above-mentioned paper [69] reconstitutes the picture of the processes taking place in cuprates. This picture supports the conclusions following from the application of the concept of DAI to these systems.

4.3 Comparison with quasi-one-dimensional semiconducting and conducting systems

The above-formulated hypothesis on the character of copper-oxygen chains in the superconducting phase of 1:2:3 compounds impelled the author to turn attention to the model compounds, investigated in considerable detail by different methods including RS spectroscopy, which might be used as examples for revealing the characteristic features of the problem of interest. Among these foremost are *trans*-polyacetylenes which long ago came to the attention of physicists and chemists working in various fields of science.

Amongst numerous experimental results obtained on this avenue of investigations, of great importance are those relating to the characteristic feature of the RS spectra of these materials. In particular, different research teams found essential changes in the spectra depending on the frequency of excited radiation, which manifest themselves in the appearance of satellites, the broadening of bands, and the one-side deformation of their profiles. The effects observed were related to the presence of a length distribution of conjugated-chain segments or the dispersion of the values of the parameter λ, which is a measure of EPI (see the review by Yacoby and Ehrenfreund [70] and the literature cited therein).

Although the observations made in these works and their structural interpretation are of great importance, another thing is nevertheless of paramount general physical interest, especially in connection with the problem of copper–oxygen bonds and their possible role in the process of HTS.

According to Peierls [71], one-dimensional systems are fundamentally unstable because of the spontaneous and periodical breaking of their symmetry associated with the generation of charge-density waves (CDW). Since this results in strong EPI, conditions for phase transformation through softening of one of optical modes are created. Commensurate and incommensurate phase transitions of this sort are considered in the literature. It is believed that they are of primary importance in solid state physics and technology as a whole, promoting, for example, the formation of dislocation defects in crystals.

Another aspect of the problem consists in the fact that CDWs modulate the frequency of an actual electron transition contributing to RS and hence radically modify the conditions of RS spectra formation, especially in resonant RS, as well as require the consideration of solitons of different types as excitations typical of the objects under investigation [72]. However, these questions of fundamental importance are beyond the scope of this review.

As model compounds, of great interest are one-dimensional systems known as 'organic metals', for example, the most extensively investigated tetrathiofulvene tetracyanodimethane (TTF TCNA) involving highly conducting weakly interacting chains in its structure, which determines a similar behavior of these materials (arising CDW, strong EPI, Peierls instabilities, and others). Hopes were pinned on these compounds in connection with searching for analogs of HTS materials in organic chemistry. A sharp increase in their conductivity at 60 K was the basis for such hopes.

An important characteristic feature of *trans*-polyacetylenes and one-dimensional 'organic metals' is the possibility of their doping in the course of synthesis, that is, introducing various elements and molecular groups into their chains. In the first case, salts of copper were successfully obtained [73]. The investigation of these objects using UV photoelectron spectroscopy showed that the copper valence in chains fluctuated between Cu^{+} and Cu^{2+} with an average ratio of 2:1. Although in this case the copper interacts with nitrogen instead of oxygen, by analogy this fact is interpreted by the author as experimental verification of both the DAI hypothesis as a whole and deductions from it concerning the structure of copper–oxygen chains in the superconducting phase of cuprates.

4.4 Phenomenon of high-frequency bands and some other effects in RS

It has long since been noted that the boundary of the line portion of the RS spectra of some single-crystal properly oriented cuprates extends to anomalously high phonon frequencies (up to $\sim 1500\ cm^{-1}$) with rather high intensities of these spectra. The effect is observed in the La_2CuO_4 type cuprates with an admixture of rare earth ions and deviations from the exact stoichiometry with respect to oxygen, in a compound $Ca_{1.8}Sr_{0.2}CuO_3$ with a copper–oxygen chain structure, and some other cases [74–78]. One feature of all these spectra is the fact that the cross sections of RS are in resonance with a transition near 2 eV corresponding to charge transfer. The effect is found if the polarization vector of incident light is oriented in the plane of layers or along the direction of chains. This is illustrated in Fig. 5.

In the literature, the high-frequency bands are usually related to the second-order scattering. To explain their extremely high intensity, a model was proposed [78] which takes into account rather strong EPI in chains favoring, in turn, the interaction of vibration modes at the boundary of fully open Brillouin zones with fully symmetric fundamental modes of chains. However, this model ignores the fact that in no cases even traces of higher-order scattering bands were found.

Let us first consider the situation with a single crystal of composition $Ca_{1.8}Sr_{0.2}CuO_3$. Since it is characterized by the presence of copper–oxygen bonds, one may start with a consideration of the pure structural aspects of the problem. Indeed, on the foregoing, it is reasonable to believe that in view of the hypothetical difference in the elasticity of Cu–O bonds along and across the chains formed by joining oxygen squares at their corners with a copper atom in the center (see Fig. 4), their associated vibrations must at least partially be separated. This is a pure dynamical effect. However, apart from this, one should also take into account a kinematical effect, which is associated with vibrations of a smaller

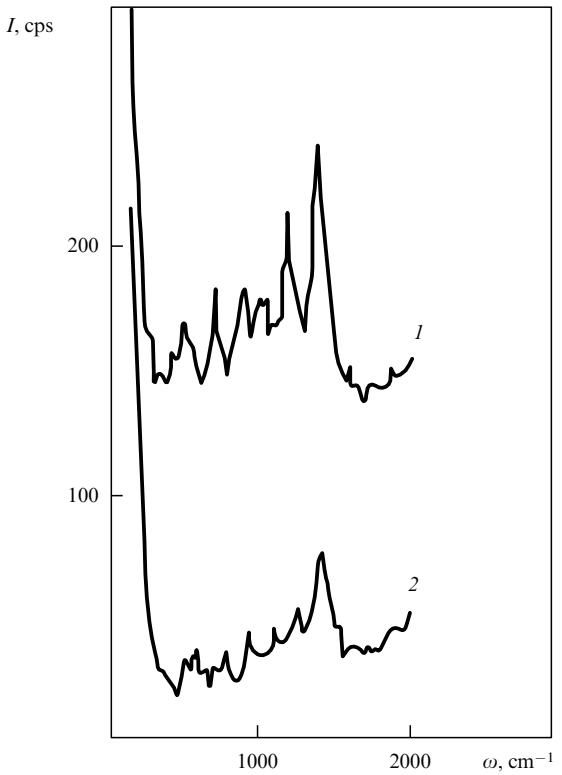

Figure 5. The line portion of the RS spectrum of a doped La_2CuO_4 crystal for the *yy* geometry: (*1*, *2*) excitation by the 514.5 and 488.0 nm radiation of an argon laser, respectively [74].

effective mass (compare a linear chain with a tape). Since both these factors act in the same direction, in combination they may induce a drastic shift of the RS spectra of this compound to higher frequencies, which is observed experimentally. Simultaneously, the very high intensity of high-frequency bands is naturally explained.

Nevertheless, such a simple interpretation of results relating to the above-considered compound (not to mention compounds without chains at all, like single-crystal $YBa_2Cu_3O_6$), have in no way exhausted the problem.

First, this is supported by the presence of specific bands in the usual vibrational-frequency range [78]. It turned out that the set of bands in the RS spectrum varies depending on the experimental geometry. Namely, when the polarization vector of incident radiation lies in the *ac* plane, vibration modes of the A_g symmetry with frequencies of 306 and 530 cm^{-1} are found in the spectrum. When this vector lies along the chains (the *b* axis), forbidden modes with frequencies of 235, 440, 500 and 690 cm^{-1} are activated. Thus, a modification of vibration modes in the whole spectral range occurs, i.e., neither of the two above-mentioned models adequately explains all results in total.

The author believes that this problem may be resolved by taking into account CDWs and their influence on RS spectra. Since under certain conditions this effect is extended to the behavior of layers [79, 80], one has a good chance of understanding why high-frequency bands are found in compounds such as La_2CuO_4 and $YBa_2Cu_3O_6$, which certainly contain no chain structures.

4.5 High polarizability of oxygen as the cause of HTS

The O^{2-} ion is nonexistent in a free state. In crystals it is stabilized by the Madelung potential. From a physical standpoint, this means that the environment of the ion strongly affects its polarizability α. As a result, the greater the covalent contribution of this environment, the higher the degree of delocalization of the 2p electrons of oxygen. In crystals such as, say, MgO, CaO or SrO, the value of α is approximately proportional to the volume V of the unit cell [81], whereas in titanates it is proportional to the third or even fourth power of V [82].

This feature of oxygen was long enough used to explain the nature and mechanism of ferroelectricity and later extended to the physics of HTS [83 – 87]. If the M partner of the $M-O$ bond belongs to the transition-group elements, bonds involving its electrons are formed. In the case of an intermediate-valence metal, an intermediate state of a resonant nature arises because of strong EPI.

A consistent development of such concepts led to the idea [86] that the contribution of oxygen p orbitals in covalent bonding must periodically vary in response to the displacements of vibrating nuclei. More recently, this effect was referred to as 'dynamical covalence' [89] and used as the basis for the mechanism of promoting hole pairing and, hence, a superconducting transition in cuprates [90].

Thus, the concept of the high polarizability of oxygen allows one to take an original approach to the problem of HTS. However, it has not escaped from notice that this model exhibits internal contradictions from the viewpoint of the nature of chemical bonding.

Indeed, assuming the polarizability α to be highly sensitive to this property and taking into account its relation to the environment of the oxygen ion, the authors who put forward this model [90] set aside the key question of what is the cause of this phenomenon. To put it differently, there is no answer to the question of what is the nature of the covalence itself. Cause and effect are as if interchanged. On the other hand, it is unlikely that a great many details concerned with the structure of cuprates can be explained and related to the whole set of data on the features of vibration spectra using so general a physical quantity as polarizability.

4.6 Domain structure of some cuprates

It was established in early research on HTS using various direct methods that a number of cuprates are characterized by submicron-scale morphology [91 – 96]. In the author's opinion, the most convincing results were obtained for 1 : 2 : 3 crystals using high-resolution electron microscopy [92]. Clusters of about 10 nm in size were found in both phases of these compounds. The occurrence of such domains was associated with spinodal decomposition, which was recently verified by an investigation of phase diagrams [93]. There is information about the presence of even smaller clusters in one system $[YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}]$ [95]. All these facts correlate with the presence of higher harmonics in RS spectra of cuprates (Fig. 6) [41].

Recently, another approach to this problem was outlined [97]. It is believed that the formation of clusters in cuprates correlates with the spatial irregularity of composition in respect of the content of copper ions having a variable valence. It was shown that the domain dimensions follow a certain distribution and are favorable for the local creation of electron pairs.

In the physics of HTS, of great importance is not only the fact of the existence of small-scale clusters, but also their spatial unidirectionality, which was well established in a number of works. This property promotes charge transfer

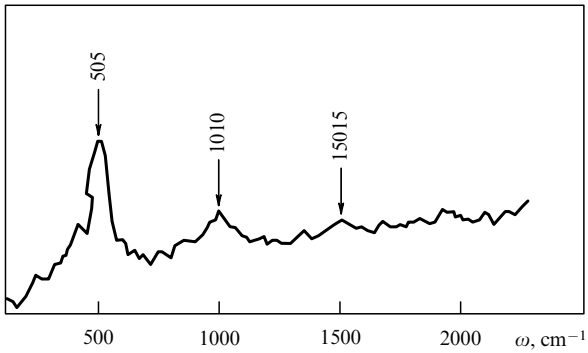

Figure 6. Resonant RS spectrum of a ceramic 1:2:3 compound in the fundamental and high-harmonic regions. Excitation by 1.06 μm radiation of a Nd:YAG continuous-wave laser. $T = 300$ K, $x = 0.85$. Higher harmonics are indicated by the arrows [41].

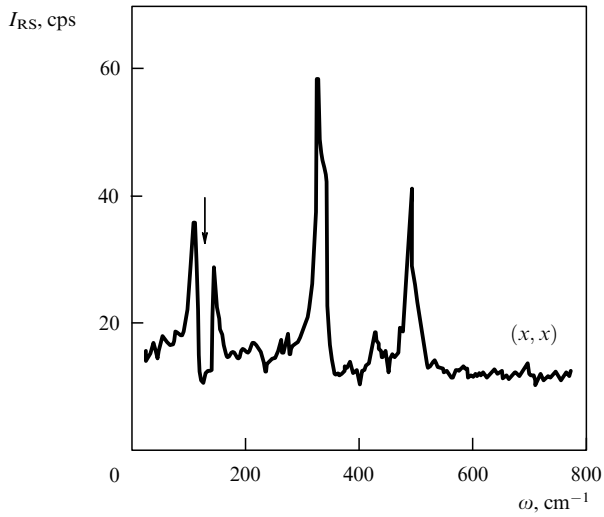

Figure 7. RS spectrum of a single-crystal 1:2:3 compound in the superconducting phase in the xx geometry at a temperature of 90 K. The arrow shows a minimum near the 120 cm^{-1} band [100].

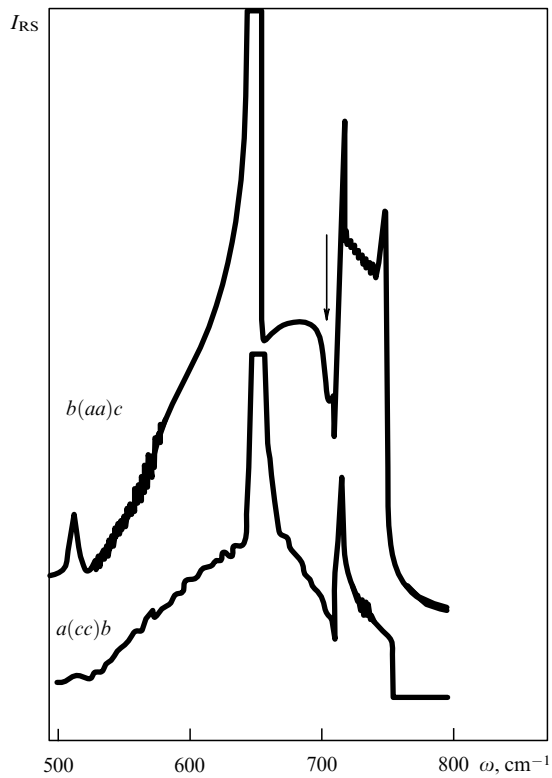

Figure 8. RS spectrum of a p-toluidine single crystal in the region of vibration of amino groups. The arrow shows a minimum near the 700 cm^{-1} band [101].

into layers and, as a consequence, enhances the concentration of carriers in them. Judging from Ref. [98], the above-indicated geometry of clusters is inherent in other solids as well.

Since clusters in cuprates are characterized by small dimensions, the presence of a more or less sharp phase boundary may be the reason for the high anharmonicity of vibrations, as indicated by direct measurements of root-mean-square amplitudes in nanoparticles of some compounds [22]. Moreover, such clusters may fluctuate, depending on the composition of cuprates, in size, shape, and 'wettability,' which adds complexity to the general picture and makes the interpretation of the results of some experiments ambiguous. This is primarily concerned with the isotopic effect.

In connection with the foregoing, brief mention should be made of the important problem of RS band profiles for cuprates of different compositions, 1:2:3 in particular. It has long been found that RS bands are often asymmetric and in a number of cases are located in the vicinity of background minima [99, 100]. A similar picture is typical of molecular crystals involving amino groups that execute inversion and rotation vibrations in a double-well potential with a resulting broadening of the corresponding bands against the background of which narrow lines of other vibrations are silhouetted [101]. Some results are presented in Fig. 7 and Fig. 8.

An analogous situation was found even earlier in SRS spectra [102]. In both cases the results obtained are correlated with the Fano profile of an interference nature. It is the opinion of many authors that in cuprates the case in point is the interference of the narrow lines of RS with the intense background of electron scattering [99, 100]. Thus, the problem reduces to the establishment of strong EPI in these compounds.

The authors of Refs [29–31] interpret their own results on the study of the RS spectrum profiles in cuprates differently, namely, in the belief that phonons with finite momenta are involved in the process and the presence of statistically distributed defects in samples is responsible for the creation of such phonons. Of course, such an approach is admissible. However, if this effect is totally or partially determined by the violation of the law of conservation of momentum, a particular role should yet be assigned to uniformly oriented domains of a submicroscopic size. It is quite possible that the dependence of the effect on the experimental geometry specially emphasized in the above-cited papers is just the fact which supports this remark. In any case it would be more properly to think of a peculiar shape of some RS bands in cuprates as being a manifestation of the combined action of both mechanisms. It seems likely that the ultimate answer to this question will be possible after additional experiments and close examination of all the results obtained will be performed.

4.7 Charge transfer in some cuprates

One of the remarkable features of these compounds lies in the fact that the superconducting properties of many of them are realized only when the crystals are doped with ions of certain metals or there is a deficit of oxygen with respect to the stoichiometry of definite structures. As already repeatedly mentioned, for the 1:2:3 type compounds the case in point is the compounds corresponding to the tetragonal and orthorhombic phases. Note that the results observed are closely related to the preparation conditions. We focus our attention only on the situation of oxygen deficit in the 1:2:3 compounds. The key problem facing experimentalists is to determine the localization of oxygen vacancies in one or other structurally specified part (chain and layer) of a sample and to extract information on the ordering state of these vacancies.

Since the problem of vacancies is connected with the physics and mechanisms of HTS, it has long attracted considerable attention. The maximum interest and accumulation of the basic experimental results date to 1987 – 1988. Nevertheless, the problem cannot be considered as being completely solved; it is still in progress, but emphasis is now on the optical methods of investigation and new approaches to interpretation of all the results.

Of crucial importance are the solid facts that oxygen vacancies localize primarily and mainly in the chain subsystem of 1:2:3 crystals. They are ordered in the orthorhombic phase and statistically distributed in the tetragonal phase [103 – 109]. These results were obtained by different methods including direct high-resolution electron microscopy. To study the dynamics of these vacancies, the methods of time-resolved spectroscopy, especially RS, were used. Relevant works are discussed in a separate section of this review.

Interesting, though to some extent indirect, information on this problem was obtained using traditional RS spectroscopy interpreting the results on the basis of the factor-group analysis of vibration modes at the center of the Brillouin zone and concrete calculations. It was found that for the orthorhombic phase of the 1:2:3 type cuprates the vibrations of the A_g symmetry with frequencies† of 116, 155, 335, 435 and 495 cm^{-1} are active in RS. In addition, the mode at a frequency of about 620 cm^{-1} is typical of this spectrum, which is forbidden by the selection rules. Its frequency and intensity are strongly dependent on the stoichiometric index x, the propagation direction, the polarization, the power of exciting radiation, and the sample temperature. All these questions were considered in detail in the literature (see, for example, Refs [110 – 116]). It should, however, be noted that in a number of cases such the classification of vibrations is a rather rough approximation, since the individual modes in fact interact with each other (see, for example, Refs [54, 117a]).

The 116 cm^{-1} mode is assigned to the motion of barium ions accompanied by destructive interference of the band with the continuous electron-scattering background. This results in the formation of minima on its high-frequency tail.

The 155 cm^{-1} mode is also assigned to the motion of barium ions in one direction and of clusters of composition $[CuO_3]$ (chain + two oxygen atoms in positions '4') as a whole in the opposite direction [117b]. It is believed that this mode plays a decisive role for the efficiency of the charge-transfer process and therefore is extremely intense in IR absorption [118], being also subject to interference with background.

† Approximate values are given.

The 335 cm^{-1} out-of-plane mode is associated predominantly with the vibration of oxygen atoms O(2) and O(3) along the c axis. Thus, this mode is a source of information on the properties and behavior of layers (moreover, in both modifications).

Judging by the fact that the 435 cm^{-1} band appears in a spectrum only when the incident radiation is polarized in the ab plane, it must also be assigned to the vibration of oxygen ions in layers. Being, however, very weak, it is analytically of secondary importance.

The subject of many works was a combined investigation of the 495 and 620 cm^{-1} modes. According to the commonly accepted point of view, the first of them is assigned to the 'respiratory' vibration in the chains where a copper ion is surrounded by four oxygen atoms O(4) and O(1). As to the second mode, in the literature it was assigned to the following factors: the anharmonic interaction of the modes at ~ 500 and 509 cm^{-1} (the latter is active only in IR spectra [119]), the violation of the selection rule for RS resulted from structural defects [120 – 122], the doubling of the unit-cell parameter c [123] and, finally, the interaction of photoexcited carriers with lattice defects [124, 125, 39].

Thus, there are quite different options on what the true reasons for and nature of a peculiar behavior of the mode at about 600 cm^{-1} are. In the following, attention will be given to one more interpretation of this effect.

Taking into account the crucial importance of the subject under discussion, it is not unreasonable to illustrate in Figs 9 and 10 how the RS spectra of some 1:2:3 type samples vary depending on their concrete composition determined by the value of the index x and the preparation conditions [126, 40]. Changes in the profile, intensity, and position of individual spectral bands are clearly seen. The spectra also contain the so-called 'extra' bands.

It is the author's belief that the model describing the dynamics of vacancies as a component part of the mechanism of charge transfer from chains to layers [127] is physically justified and workable. It is concerned with a separate link of a tape formed by Cu(1), O(1) and O(4) ions, which is depicted in Fig. 11.

An essential feature of the idea suggested by Gasparov et al. [127] is the assumption that apical oxygen atoms move in an *asymmetric* double-well potential having two minima of different depth. It is further believed that one of the minima corresponds to the vibration of the O(4) ions and the other to the vibration of the O(1) ions. Both ions may overcome the potential barrier by tunneling or activation. The latter occurs owing to change-over (jumps) of vacancies and determines the temperature effects which show themselves in RS spectra as frequency shifts and redistributions of intensities for the 485 and 620 cm^{-1} modes. Estimates of both ways of overcoming the barrier taking into account the large cubic anharmonicity were made. It was finally assumed that the last circumstance may be the reason for the appearance of bands due to second-order scattering, which was borne out experimentally. However, the authors did not consider the possible contribution of electrooptical activity to this effect.

Thus, even in its original form this model allows one not only to interpret a number of well-known facts, but also predict new effects. Nevertheless, there is no doubt that it needs further development. It is the author's opinion that the model has a number of weak points. These are the absence of a direct relationship between the vacancy jumps and the

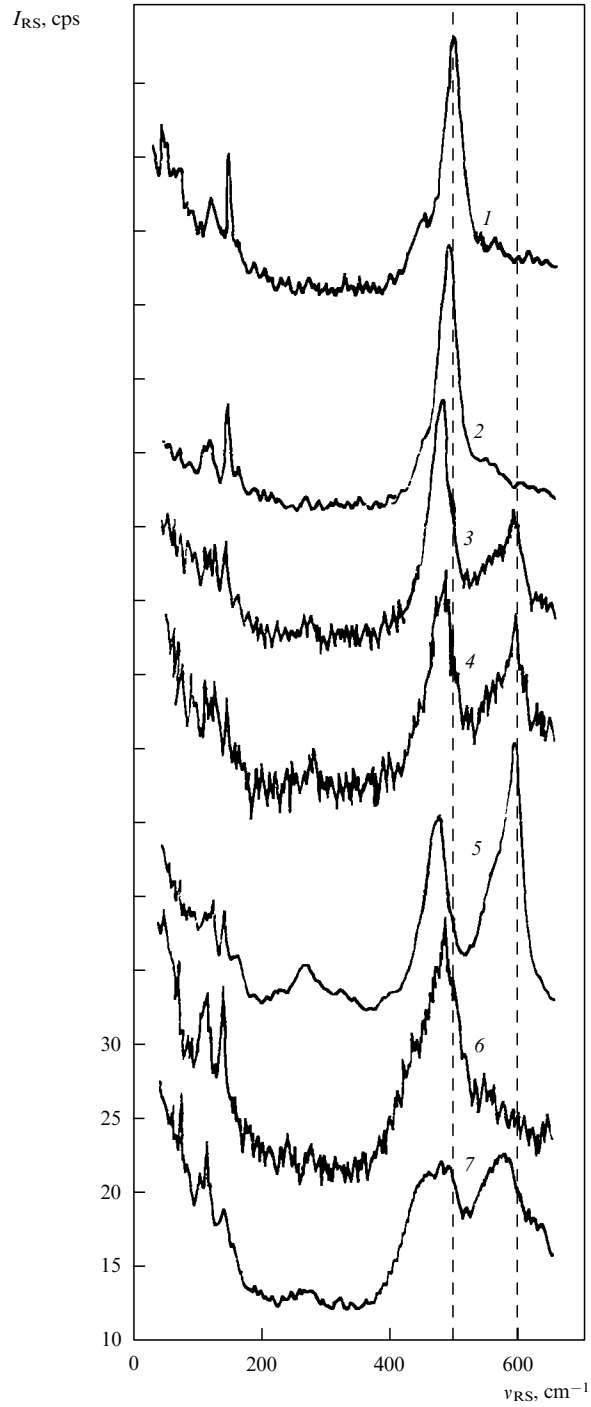

Figure 9. RS spectra of single-crystal $YBa_2Cu_3O_x$ depending on composition and temperature: (*1*) $x = 7$, $T = 23\,^\circ$C; (*2–5*) $x = 6.6$, $T = 23$, 168, 225, 300 °C, respectively; (*6*, *7*) $x = 7$, $T = 500$ and more than 500 °C, respectively [126].

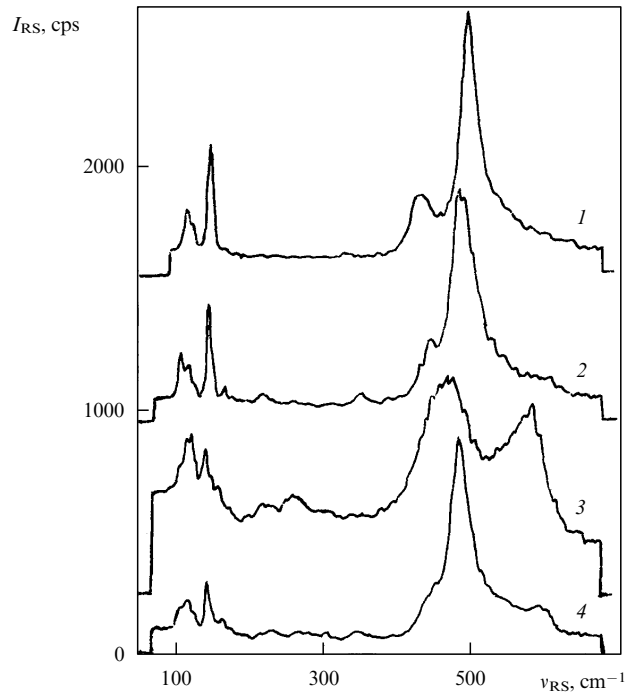

Figure 10. RS spectra of single-crystal $YBa_2Cu_3O_x$ for *cc* polarisation: (*1*) $x = 6.9$, $T = 50\,^\circ$C; (*2*) $x = 6.5$, $T = 50\,^\circ$C; (*3*) $x = 6.5$, $T = 250\,^\circ$C; (*4*) $x = 6.5$, $T = 50\,^\circ$C [40].

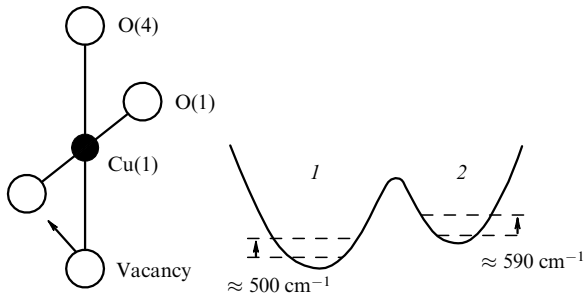

Figure 11. Model of a double-well potential for a 1:2:3 crystal in the superconducting phase. A chain-structure fragment is shown at the left [127].

arrangement of vacancies as well as the lack of any notions about the nature of the asymmetry of the potential in which the apical O(4) ions move. These questions seem to be of great importance not only for revealing the details of the charge-transfer mechanism in the compounds discussed (which is a key problem by itself), but also for predicting the possibilities of forcing relevant processes.

We recall once again that it is reasonable, on previous grounds, to consider rather lengthy segments of chains in cuprates as having the structure of conjugated copper–oxygen bonds. Owing to the above-mentioned physics of one-dimensional chains, CDWs are bound to arise in them. As a result, they become a source of carriers or, according to the accepted terminology, their reservoir [128, 129].

The side Cu(1)–O(4) bonds serve the other function: according to the model put forward in [127], they are, along with oxygen vacancies, a sort of sluices which 'discharge' the carriers into conducting layers and work in tandem with double-well potentials whose parameters directly depend on the composition and fabrication technology of samples and, hence, determine the possibility of overcoming the barriers. The first role in this process we ascribe, contrary to Ref. [127], to the vibration of the ionic group Cu(1)–O(4)–Cu(1) with a frequency of about 500 cm^{-1}. This conclusion stems from the following facts.

Using the data on the ionic radii of Cu^{1+}, Cu^{2+} and O^{2-}, it is easy to show that in the ionic approximation the lengths of

the $Cu^{1+}-O^{2-}$ and $Cu^{2+}-O^{2-}$ bonds are 2.42 and 2.38 A, respectively [58]. At the same time, the averaged values of these bonds measured by different authors for cuprates depending on the oxygen stoichiometric index x show that the Cu(1) – O(4) bonds are much shorter ($\sim 1.8-1.86$ A) and the Cu(2) – O(4) bond lengths lie in the range 2.3 to 2.45 A [128, 129]. If the covalent radii are used, a close agreement of their sum with the lengths of the shorter bonds is achieved. All this taken in combination shows that the Cu(1) – O(4) bonds are predominantly covalent, whereas the Cu(2) – O(4) bonds are ionic.

Thus, considering the double-well potential as formed due to the motion of the Cu(1) – O(4) – Cu(2) ions and taking into account the different nature of the corresponding bonds, one can explain, at least hypothetically, its asymmetry. In addition, of great importance is the fact that such a consideration is centered on the final stage of the process, when paired carriers are created in the layers.

It is a matter of common knowledge that the value of any detected signal which contains information on HTS depends on the concentration of the carriers of this process. This value is also determined, among other things, by the synchronism of the charge-creation and charge-transfer mechanisms. Therefore, a light field can play a great role in stimulated scattering.

Let us suppose that rather intense pulses of light are incident on a system, inducing SRS, and, hence, providing phase ordering of vibrations. Under the action of these processes, originally incoherent thermal vibrations acquire a temporal and spatial coherence. On the other hand, under such conditions large anharmonicity of vibrations is induced, which results in a more or less sharp increase of the probability of overcoming the barrier, no matter which mechanism (tunneling or activation) is predominant. As a result, the charge transfer can become an avalanche-like process. Such a situation would naturally be expected at the instant the exciting pulse of light is applied. It is likely that it was already observed in quantum-beat experiments. It will be the subject of consideration in the last section of this review.

In closing this section, two additional remarks are necessary. Although the structural interpretation of the mechanism of HTS suggested seems to be reliable, it under no circumstances should be considered as universal. Indeed, among the HTS materials there exist such, for example, bismuth-based compounds, that contain no chains in their structure at all. Another remark concerns the hypothesis of the high polarizability of oxygen as the cause of HTS. There is no doubt that this property plays a great role in structural instability of various systems, in particular in the context of the problem of their ferroelectric behavior. As to HTS, concrete model calculations give a clear indication of the presence of expected anomalies in the vibration RS spectra only in special cases. One such case, as far as the author knows, is the 155 cm^{-1} band typical of the 1:2:3-type cuprates. It is this band for which a sharp increase in IR absorption during phase transition from the dielectric to the superconducting phase was observed [118].

There is no clear understanding of the microscopic mechanism of this effect. Its treatment on the basis of the concept of dynamical covalence is unconvincing, since it is doubtful that the latter may change essentially even for considerable nucleus amplitudes.

4.8 Role of the anharmonicity of vibration modes and the nonadiabaticity of states in HTS

In a number of papers concerning the study of HTS using RS spectroscopy, attention was drawn to the absence of rigorous characteristicity of many vibrations in cuprates. Assuming that mixing affects fully symmetric vibrations involving oxygen atoms, Batistic et al. [117a] have shown on the basis of a simple physical model that this effect has a strong influence on the character of isotopic substitution.

An obvious reason for the mixing of all, without exception, modes in cuprates is their more or less pronounced anharmonicity. This is especially true for those of them that are associated with the motion of apical oxygen in a double-well potential.

In this section, attention is centered on the problem of the interaction of fully symmetric and non-fully symmetric vibrations and its influence on the shape of RS spectra as the source of information about HTS. Besides, the role of the non-rigorous adiabaticity of optical processes in cuprates, which probably reflects on the effect of isotopic substitution, will be discussed.

As is known, in its original form the model of the process of RS, proposed by Albrecht [25, 26] and used by the author of this review separately describes the behavior of all fully symmetric vibrations and those of non-fully symmetric vibrations that are active in the mixing of different upper electron states, respectively. It should be noted that this property is only realized under special conditions of resonant excitation of RS spectra. Besides, this model holds only for low-dimensional systems, so that all comparisons are made on the molecular level. Because of this, it makes sense first to consider the consequences of possible interactions between different-symmetry vibration modes on the molecular level and only then to extend them, with a certain reservation, to cuprates.

The goal of such experimental and theoretical investigations, which were made time and again for relatively simple molecules, consisted in fixing the violations of the Franck – Condon distribution of intensity and other anomalies adequately reflected in RS spectra at different vibration-interaction parameters.

For example, attention was drawn to the fact that the vibronic induction of a forbidden electron transition in benzene molecules results in spectral structures composed of the mixing non-fully symmetric vibration ω_b and the progression of the full-symmetry vibration ω_a which follow different selection rules [130]. Two cases of the interaction between these vibrations through the cubic anharmonicity of potential are considered.

The first case is realized when there are two mixing vibrations ω_b and $\omega_{b'}$ of the same symmetry. In such a situation $\omega_b + n\omega_a$ and $\omega_{b'} + (n \pm 1)\omega_a$ structures are formed. They are able to break the ideal picture of the Franck – Condon distribution in spite of the fact that the matrix element of the corresponding transition including anharmonicity in the form of $Q_a Q_b Q_{b'}$ is rather small because the anharmonicity constant is usually less by an order of magnitude than the distances between the components of the structure. The other case of interaction, being of more general interest, relates to the mixing of the $2\omega_b + n\omega_a$ and $(n+1)\omega_a$ states through the cubic term $Q_b^2 Q_a$. In both situations the mirror symmetry between the effects of emission and absorption breaks down, which is proved by direct experiments. According

to theory, this, indeed, must be the case for both types of interaction.

Clearly, these effects must be adequately reflected in the spectra of resonant RS, especially in the case of cuprates if these latter have a low-dimensional cluster structure.

In the above discussion, special cases of coupling between the fully symmetric and non-fully symmetric modes were considered, when the optical transitions are determined (activated) by vibronic interaction. In Ref. [131], a universal model of this effect was proposed. It is believed that this effect originates from the difference in the equilibrium distances of two upper electron states, one of which in the absence of vibronic coupling is related to a forbidden transition and the other, to a close, allowed source of intensity in the corresponding transition. The problem is solved with the assumption that both adiabatic and nonadiabatic interactions exist between them. Quantitative estimations show that the ratio of the intensities of emission and absorption lines may be considerably distorted. It is emphasized that taking into account anharmonicity leads to an enhancement of this effect.

Irrespective of the characteristic features of a concrete model describing the vibronic activation of forbidden electron transitions and the extension of the results to RS, of great importance is due consideration of the number and symmetry of all states as well as the efficiency of mixing itself. Without going into details, we will only note that these factors determine the form and multiplicity of potentials and, hence, the character of optical transitions and resonances in RS. The above can be illustrated by examples from [132, 133].

In the first paper, Natsume theoretically examined two cases: (1) all three electron states are nondegenerate: (2) the upper electron state, from which an intensity is adopted at transitions, is doubly degenerate. It turned out that even without orbital degeneracy (in the first, more simple case) there were a number of important features. In particular, it was shown that in the adiabatic approximation an increase in the dimensionless parameter η that characterizes the efficiency of mixing ($\eta = 2b^2/\omega^2 w$, where w is the energy difference between the two excited states), leads to an increase in the curvature of the upper-state potential and a decrease in the lower-state one, causing a double-well form of the potential curve. The curvature of both wells was found to be independent of the interaction force. This signifies a symmetry of the potential. This picture, however, may change in going to a nonadiabatic approximation. In the second case, the potential takes a triple-well form. The results of calculations [134] show that resonant RS spectra behave in a like manner.

From the above discussion, a general conclusion can be made that the form of the potential of an intermediate (virtual) state plays a primary and predictable role in the elementary act of RS. This problem was recently theoretically analyzed in the most general case using a temporal representation of the process of HTS [135]

It is helpful to distinguish two cases of interaction of light with substance: usual (two-photon) RS and hyper-Raman scattering (HRS), the process in which not one, but two quanta of exciting radiation are drawn into RS. With consideration for a scattered quantum, this is a three-photon process.

It is not difficult to conceive that the latter may exhibit two types of resonance, with one-photon and two-photon absorption (OPA and TPA, respectively), which in addition can be realized simultaneously in one act of HRS. Furthermore, it is amply clear that each absorption level correlates with the unique character of its associated potential. This is bound to lead to fundamental differences in the processes of RS and HRS when realizing resonant excitation of both types of spectra.

To clarify this question, a theory of resonant HRS that was developed for the Albrecht model [136] can be used. It follows from this theory that it is predominantly the term A (an analog of the corresponding term in the Albrecht formulas), which exhibits a sharper frequency dependence for fully symmetric vibrations, that will increase as the frequency of incident radiation approaches an intense band of OPA or TPA with a relatively large cross section. In the case of a resonance with weak bands of OPA and TPA adjacent to one or more strong bands, the contribution of the term A to scattering may be small in comparison with the term B which describes the enhancement of non-fully symmetric vibrations active in mixing.

Thus, a wide variety of formation conditions arise for all bands inherent in a given system, that is, a rather complex picture on the whole. Consequently, one would expect a discrepancy between the behavior of resonant RS and HRS spectra, especially in studies of the frequency dependence of band intensities, that is, excitation spectra.

Since for excited electron states the intersection or at least the proximity of the potential curves is the rule rather than the exception, the question arises of how their interaction is realized. In theory, both the 'adiabatic', that is, an infinitely slow closing of the curves, and the case when the rate of closing is finite and the resulting states are approximated by a linear combination of the initial ones are considered. Apart from the already cited work [135], this problem, as applied to the description of the process of RS, was considered in a series of early theoretical publications [137–143, 131]

As is known, there also exists a notion of the nonadiabaticity of vibration modes, that is, a situation when the motions of electrons and some vibrational degrees of freedom of nuclei cannot be separated. This effect is usually small and proportional to $(m/M)^{1/2}$ where m and M are the masses of an electron and a nucleus, respectively. However, in special cases there is a necessity to take into account the departure from adiabaticity. Such a situation arises in the case of cuprates when the distance between two potential wells is close to the energy of a vibration quantum. Recently, a general theory of phonon nonadiabaticity was developed with orientation to the further study of superconducting materials [144].

According to [137], in the simplest case of two noninteracting vibration modes, the nonadiabaticity of electron states can properly be taken into account with the use of additional factors $\Delta \mp h\omega$ in the denominators of the term B of the vibronic theory (Δ is the energy difference $E_e^0 - E_s^0$ measured from the zero-point energy, and $h\omega$ is the energy of the vibration active in RS). The expression for this term takes the form

$$B = \frac{\langle g|R|e\rangle\langle s|R|g\rangle\langle e|\mathrm{d}v/\mathrm{d}Q|s\rangle\langle 0|v\rangle\langle 0|v\rangle\langle v|Q|1\rangle}{(E_v - h\nu_L - \mathrm{i}\Gamma_e)(\Delta - h\omega)} + \frac{\langle g|R|s\rangle\langle e|R|g\rangle\langle s|\mathrm{d}v/\mathrm{d}Q|e\rangle\langle 0|Q|v\rangle\langle v|1\rangle}{(E_v - h\nu_L - \mathrm{i}\Gamma_e)(\Delta + h\omega)}, \quad (4.1)$$

where Q is the normal coordinate of the vibration mode which is active in resonant RS and v is the number which determines

the occupancy of an excited vibrational energy level. The matrix elements of transitions are written as $\langle g|R|e\rangle$ and $\langle g|R|s\rangle$, where g, e and s stand for the ground and two interacting upper electron states, respectively. The expression $\langle e|\mathrm{d}v/\mathrm{d}Q|s\rangle$ determines the extent of vibronic coupling of the adiabatic states e and s. Previously it was designated as h_a. For the sake of simplicity, the decay factor Γ_e is considered to be independent of v. E_v is the vibronic energy of the state which is in resonance with the incident quantum $h\nu_L$.

Expression (4.1) becomes more complicated for multimode systems. This can be of great importance for the quantitative interpretation of RS spectra [137]. It should be noted that far from resonance the contribution of adiabaticity to scattering drops sharply. In both cases this contribution depends on the orientation of crystals and the polarization of incident radiation.

The above-discussed questions directly concern the peculiarities of the isotopic substitution of oxygen atoms in cuprates. It has already been mentioned that in a series of early works performed by different research teams, the parameter α characterizing the relative variations of T_c was found to be small in some cuprates. This fact became an argument against the concept of a predominant contribution of the phonon mechanism in HTS. However, more recently it was recognized that the value of α is strongly dependent on the concentration of carriers and may considerably exceed the value (~ 0.5) which was assigned to it by the BCS theory. On the other hand, it was noted that its minimum value corresponds to the maximum value of T_c.

These observations, including the last paradox, were interpreted in detail in Ref. [145], where the nonadiabaticity of the vibration motion of apical oxygen atoms in cuprates with a chain subsystem was likely to be taken into account for the first time. In this case we deal with a double-well potential formed by two very closely spaced electron states, so that the total eigenfunction of the system cannot be written in the form of a simple product of its electron and vibration parts. This fact results in the dependence of the process of charge transfer from chains into conducting layers on the mass of the nuclei. Eventually, such an analysis allows one to obtain two expressions describing the effect of isotopic substitution:

$$\alpha = -\frac{M}{T_c}\frac{\partial T_c}{\partial n}\frac{\partial n}{\partial M}\,, \tag{4.2}$$

$$\alpha = \gamma\,\frac{n}{T_c}\frac{\partial T_c}{\partial n}\,, \tag{4.3}$$

where n is the charge carrier concentration and γ is the proportionality factor which is only weakly dependent on M on a logarithmic scale.

It is of great importance that in Ref. [145] a key role of the Franck – Condon intensity distribution in these processes was established. This puts the conditions of its formation in the forefront, and its dependence on the anharmonicity of vibrations in particular. Besides, the theory is based on the model of two potentials which are close in magnitude but differ essentially in shape. In Ref. [143], commenting on this assumption, the authors appeal to the Jahn – Teller effect complicated by the peculiarities of a local field, since in an ideal situation the split components must be symmetric. From our point of view, the cause of asymmetry is the different character of the bonds of the apical oxygen atom with the Cu(1) and Cu(2) atoms (see Section 4.7). Being more common and natural, such an approach does not need any additional assumptions and hypotheses.

4.9 Collective modes in the spectra of chain structures

Among such systems, modeling many HTS materials, are *trans*-polyacetylenes and some other polymers, as well as 'organic metals'. Of particular interest are materials which may be doped by atoms and groups (like iodine, sodium, AsF_5, SO_3, etc.) playing the role of donors or acceptors of electrons. It is better if the same effect is achieved using the procedure of prior photoexcitation to create metastable states. In any case, this leads to lifting the prohibition of some IR transitions, which allows one to obtain new information on the structure of the objects under investigation and associated processes. It is likely that analogous effects were also observed in the studies of cuprates; hence our special interest to this question. Note finally that superconductivity arises in some 'organic metals' as a result of inserting donors into chains.

Turning first to *trans*-polyacetylenes, we recall that their resonant RS spectra exhibit a number of interesting features. Namely, as the wavelength of exciting radiation moves from the visible to the ultraviolet region, their bands are broadened, and eventually distinct satellites appear on the side of greater vibration frequencies, with a change in relative intensities. In early works these effects were assigned to the presence in samples of chains of conjugated bonds of different length. This assumption was correlated with different positions of the actual electron transition and hence the different excitation frequency dependence of the intensity of resonance bands.

As is seen in Figs 9 and 10, the RS spectra of the samples of 1:2:3 cuprates whose composition was determined by the oxygen content exhibit, in general, similar features. All the more remarkable example is given by a single crystal of the 1:2:3 dielectric phase investigated recently by the RS spectroscopy method in connection with the problem of photogeneration of HTS [146]. The sample was subjected to pulses of IR radiation. Under this conditions, a frequency shift of the 50 cm^{-1} RS band was observed, as well as an enhancement of a number of the initially weak bands 'forming' a pedestal for the 500 cm^{-1} band, and the appearance of about ten new bands in the frequency range 400 to 600 cm^{-1} as compared with unirradiated crystals.

It is not inconceivable that the results obtained recently by Fantini et al. [147] fall into this category of effects. The authors investigated the behavior of superconducting ceramic 1:2:3 samples when heating the sample to very high temperatures.

Thus, it may be assumed that these effects have a common nature in cuprates and *trans*-polyacetylenes. As to RS spectra, their behavior is linked to the so-called amplitude modes (AM) in quasi-one-dimensional chains, similar to those described by Peierls [71], taking into account their action on the corresponding electron transition. Instead of the length distribution of conjugated-bond segments, a physically more substantial parameter — the distribution over the values of EPI constants is introduced.

The theoretical description of RS spectra is based on the following model. A multiphonon system with frequencies ω_n^0 ($n = 1, 2, \ldots, N$) corresponding to vibrations of the bonds that are made by σ electrons is considered. The motion of π electrons and EPIs due to this motion are related to the formation of CDWs in chains. As a result, AMs arise and a

renormalization of vibrational frequencies from ω_n^0 into ω_n^R takes place. These processes are analyzed in the adiabatic approximation when $\omega_n^0 \ll 2\Delta$, where 2Δ is the energy of the corresponding electron transition. The cross section of resonance RS is written as

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} \sim \left| f\frac{h\omega_L}{2\Delta}\right|^2 I_m \frac{D_0(\omega)}{1+(1-2\bar{\lambda})D_0(\omega)}\,, \tag{4.4}$$

where $\bar{\lambda}$ is the effective constant taking into account, apart from the EPI constant λ, the electron–electron interaction ($\lambda = \bar{\lambda}$ for Peierls chains); f^2 is the intensity of resonance RS bands depending on $h\omega_L/2\Delta$; $D_0(\omega)$ is, according to accepted terminology, the 'dressed phonon propagator,' which has the form [148, 149]

$$D_0(\omega) = \sum_{n=1}^{N} \frac{\lambda_n}{\lambda} \frac{(\omega_n^0)^2}{\omega^2 - (\omega_n^0)^2 - \mathrm{i}\delta_n\omega}\,, \tag{4.5}$$

where $\mathrm{i}\delta_n\omega$ is the decay factor. The remaining designations are as before.

Apart from AMs, quasi-one-dimensional chains are characterized by other collective excitations, the so-called phase modes (PM), associated with the modulation of the vibration-mode phases resulting from the interaction of periodic motion of nuclei and electrons with CDWs [148]. This optical phenomenon manifests itself in IR absorption as the activation of bands formally forbidden on symmetry considerations. They are polarized along the chains and therefore are not observed in spectra for perpendicular polarization. The theory developed in Ref. [149] ascribes to them the same form of a phonon propagator as for AMs.

For organic conductors, this effect has long been described by different research teams. As an example, we refer to paper [150] in which the authors intuitively interpreted their results as a manifestation of strong EPI. More recently such observations were made in studies of some organic polymers including *trans*-polyacetylenes subjected to controlled doping by various groups of atoms or photoexcitation. The true nature of the effect may be interpreted on the basis of the concept of collective excitations, as was shown in Refs [151, 152].

The processes occurring in samples as a result of photoexcitation are amenable to an obvious interpretation. It may be believed that photoexcitation leads to the generation of point charge defects in chains and, hence, to violation of the selection rules for IR transitions because of the considerable distortion of local symmetry. This inevitably results in the activation of modes with A_g symmetry. It is also easily understood that the physical cause of this effect is the violation of the translational symmetry of Peierls chains. This predetermines the dependence of the effect on the lifetime of the corresponding state, that is, eventually on the magnitude of the point potential. These questions will be considered in another section of this review using experimental data.

The salts of 'organic metals' in which a charge transfer along chains takes place began to be studied intensely when superconductivity at a temperature of 2 K under hydrostatic compression was found in one of them [153]. This was followed by a number of publications on the same subject concerned with studies of some related compounds doped by various ions. To identify structural modifications of samples, resonant RS was used. For example, it was found [154] that for the superconducting phase of one of the samples, the formation of a commensurate superstructure was typical. This superstructure revealed itself through the splitting of the fully symmetric mode of I_3^- ions introduced into the chains. Kinase and Kavata [155] point toward a possible association of HTS with the formation of incommensurate structures in cuprates.

At first glance it would seem that the above-listed facts are in a rather poor correlation with the general approach put forward in this review in which primary emphasis is placed on the role of the chain-structure subsystem of cuprates. In fact, this is not the case. It is well known that collective modes are equally inherent in conducting layers; however, they may exist only under certain conditions. This rather complicated question was discussed in many original papers and reviews. For example, on the basis of a comprehensive analysis of the problem, Bulaevskiĭ [80] came to recognize that CDWs and their associated effects and structural transformations in layered compounds are, in particular, possible if flat segments exist at the Fermi surface. For one-dimensional chains, all the complex of effects observed is an appropriate and universal result, since it reflects their immanent peculiarities and properties [71].

In conclusion, it should be noted that a general theory of RS by AMs for superconductors characterized by the existence of CDWs has already been developed [156]. Without CDWs, 'effective densities' describing RS are determined by PMs and therefore contribute to just this process, whereas AMs are not observed in scattering. However, Littlewood and Varma [157] have shown that this is not the case in reality and CDWs are determined by AMs as well, but the energy of the corresponding states is close to the double energy gap 2Δ. In Ref. [156], the different channels of the process of HTS are considered in detail taking into account the crystal symmetry and the concrete shape of the Fermi surface†.

5. Distribution and motion of oxygen vacancies, and their interaction with the crystal lattice

Since the above-mentioned problems are of crucial importance for an understanding of the physics of HTS and its connection with the structures of the objects under investigation, they drew attention immediately after the discovery of this effect. Different experimental methods, including the traditional RS spectroscopy, were used. After Cava [158] proposed a model of charge transfer into conducting layers, this line of investigation was given new impetus.

Prominent among these investigations was an experimental work [159] in which the vacancies of chain oxygen in thin films of 1:2:3 cuprates were subjected to an applied constant voltage, and the result of processes occurring in the films was determined with the use of local RS spectroscopy and optical microscopy.

The idea of such experiments was as follows. At the time of their performance, it was unclear what was the true mechanism of vacancy ordering: does it take place over all sample volume or through the formation of microregions of differently oriented phases, so that the resulting effect is determined by their distribution? If the latter mechanism is correct and the microregions are large enough and have phase boundaries and microlinks, the behavior of the sample must be critically sensitive to the applied voltage. This was indeed

† The author is grateful sincerely to E Yu Perlin for enlightening the difficult theoretical aspects of the problem.

the case. The authors [159] succeeded in observing the character and dynamics of aggregation of chain-oxygen vacancies in basal planes and showed that they dealt with a threshold process with the state of ordering directly depending on the current density.

Films of 140 – 210 nm in thickness were fabricated by evaporation of substance using pulses of laser radiation. RS spectra were excited by the 514.5 nm radiation of an argon laser in different places on the films along the c axis. The radiation power was no more than 3 mW. The light-spot diameter was 1 μm.

Thus, the results of the latter work [159] are of great importance in connection with the problems of the vacancy-ordering dynamics and the formation of large-scale clusters in cuprates.

To solve the first problem, much information can be obtained through the use of time-resolved RS spectroscopy. The first work on this subject was probably made in 1990 [49].

In all investigations of this sort, two pulsed radiations of different frequency and intensity are used. One serves to create a nonequilibrium concentration of scattering centers, the other serves to probe these centers. Both radiations are separated by a controlled time interval, which enables one to follow the course of the processes.

In this case, the function of the more intense radiation is to control the concentration of vacancies at the crystal surface. Owing to this, there is a possibility to follow the movement of vacancies from the volume of a sample to its periphery using RS spectra excited by much more weak radiation. It turns out that this process proceeds rather rapidly (for less than 5 ms), whereas the final state remains over a period of more than 1 min. The results obtained allowed one to assume that the diffusion of vacancies to the crystal surface depleted of oxygen up to the composition of the nonconducting phase was accompanied by their jumps from one crystallographic site, O(1), to another, O(5). This process was found to correlate with the intensity and frequency of two vibrations: 500 and ~ 580 cm^{-1}. From this fact, a conclusion was drawn that there exists a strong anharmonic coupling between the first mode and the IR mode of the chain structure.

Thus, the work [49] was the first where quantitative data on the dynamics and character of vacancy ordering in the bulk and at the surface of a sample were obtained.

Since up to the present time lively discussion about the role of chain oxygen atoms in the mechanism of HTS is still in progress, of great interest are the results obtained by Singh et al. [42] in studies of resonant RS excited by nanosecond pulses. One idea was to realize selective disordering of oxygen vacancies in chains. To solve this problem, an ingenious method using the thermal action on a sample of exciting light pulses themselves was implemented. Assuming the Cu(1) – O(1) bonds to be relatively weak, the authors obtained the desired results by fast heating the sample with these pulses. This provided the creation of a nonequilibrium concentration of selectively disordered chains. In this case the rate of heating and cooling is many orders of magnitude greater than in the usual experiments on quenching samples in liquid nitrogen. As a consequence, they succeeded in separately observing the origin and kinetics of the process of HTS localized in layers at the expense of the disordering of chains, which could be inferred by broadening and blurring of the associated vibration bands. Some of the results obtained are illustrated with the spectra presented in Fig.12.

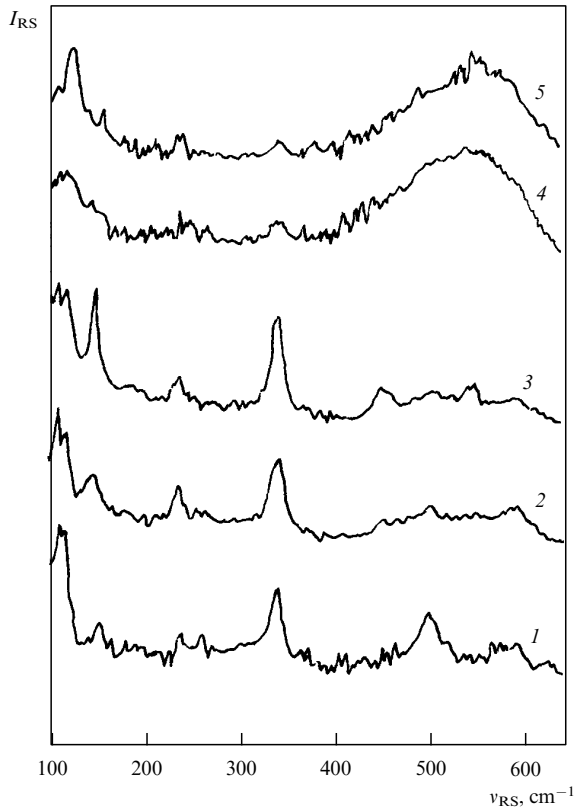

Figure 12. RS spectra of the $YBa_2Cu_3O_7$ film before and after the action of the different-power radiation of the XeCl laser: (*1*) initial film, (*2 – 5*) powers of 90, 150, 250 and 400 mJ cm^{-2}, respectively. Sharp broadening of the chain-vibration modes, indicating structural disordering, is seen [42].

Thus, it was shown for the first time that the ordering of oxygen vacancies in the chain structure of cuprates is not a necessary condition for realization of HTS. This conclusion is, in general, consistent with the assumptions on the role of CDWs, since they, as was mentioned above, may arise directly in conducting layers.

In connection with the problem touched upon in Ref. [42], it is pertinent to discuss the results obtained recently by Osquiguil et al. [160]. These authors conducted direct measurements of the photon-induced increase of T_c and the conductivity of a film oriented along the c axis depending on the oxygen content in the limits $6.4 \leqslant x \leqslant 7$. Both parameters decrease in magnitude with enrichment of the films in oxygen and becomes zero at $x = 7$. At the same time, the x-dependence of T_c is similar to that observed in the case of ordering of vacancies for a 1 : 2 : 3 crystal. Thus, it may be assumed that vacancy ordering is just the factor which determines the metastable characteristics of the effect.

Turning back to the problem of the influence of photo-excitation on vibration spectra, it should be noted that for cuprates this effect was apparently observed for the first time for La_2CuO_4 and assigned to strong EPI [161]. It was also reported [162, 163] that two phonon modes at 435 and 510 cm^{-1} with A_g symmetry, associated with the motion of oxygen ions transversely to Cu – O layers, were found in the IR-induced spectra of the tetragonal phase of 1 : 2 : 3 samples. Analogous observations were made by Kim et al. [164] and related to the creation of extra carriers in the conducting layers. Even more radical conclusions were drawn by

Mihailovic and Foster [120] who believe (as the previous authors) that according to their data on RS and IR absorption in 1:2:3 compounds, photogeneration is accompanied by the local deformation of their crystal lattice near the phase transition, which results in the formation of polarons and bipolarons. The effect is assigned to the anharmonic interactions of the 485 and 510 cm^{-1} vibration modes active in RS and IR spectra, respectively. The authors believe that this interaction is the cause of the asymmetry of the double-well potential.

In our opinion, the next important step in using resonant dynamical RS spectroscopy to the problem of HTS was recently made in Ref. [166]. The authors posed and solved the problem of studying EPI of nonequilibrium carriers using the results of measurements of the relative intensity $I_{\text{Stokes}}/I_{\text{anti-Stokes}}$ in the picosecond mode of excitation. The objects of this unique experiment were 1:2:3 films. Two essentially different vibrations with frequencies 340 and ~ 500 cm^{-1} were studied. The exciting radiation served simultaneously for photogeneration of extra carriers whose concentration was controlled by the pulsed pumping power. It was found that the last-mentioned vibrations interact with the lattice in a qualitatively different manner: for the 500 cm^{-1} vibration associated with the motion of apical oxygen atoms, the nonequilibrium concentration of excited phonons increases (with a break near the phase transition) and for the 340 cm^{-1} vibration, on the contrary, decreases. This result is related to strong EPI in the first case and the creation of lattice polarons.

When investigating the frequency dependence of resonant RS, a well-marked relation of these spectra with one or other excited electron state was long ago noted. This fact was mentioned in Section 4 concerned with a high-frequency band phenomenon. The results obtained when exciting RS in different zones of structured absorption bands (in the visible and near infrared regions of the spectrum) are very instructive and may be uniquely interpreted [41].

In Fig. 6, the RS spectrum of a ceramic 1:2:3 compound of the last type was presented. The characteristic feature of this spectrum is the appearance of very intense harmonics of the 505 cm^{-1} vibration. This is decisive evidence that in this case we are dealt with the small-sized local centers of scattering.

A completely different situation was observed when exciting the RS spectrum of the same samples by the 514.5 nm radiation of an argon laser. As is seen in Fig. 13, the spectrum is formed by a different set of vibration modes. The main feature is the total absence of higher-order harmonics. Hence, it corresponds to a lengthy crystal structure, which precludes the presence of the Franck–Condon mechanism of RS.

As to the spectrum determined by small-scale heterogeneities of a sample, the authors of [41] relate its specificity to the vibrations of apical oxygen atoms. Oxygen vacancies can also contribute to these heterogeneities. In any case, these facts are amenable to hypothetical interpretation.

Problems arise with related experimental data. For example, it is reported [167] that a single crystal of 1:2:3 without twinning exhibits a narrow resonance at 2.2 eV along chains, which manifests itself in enhancement of two vibration modes forbidden by the selection rules for RS. Two mechanisms for this effect are suggested: the first mechanism takes into account the special properties of the Cu(1) $d(yz)$ state of copper in chains, the second is based on the influence of oxygen vacancies. The first mechanism is preferable.

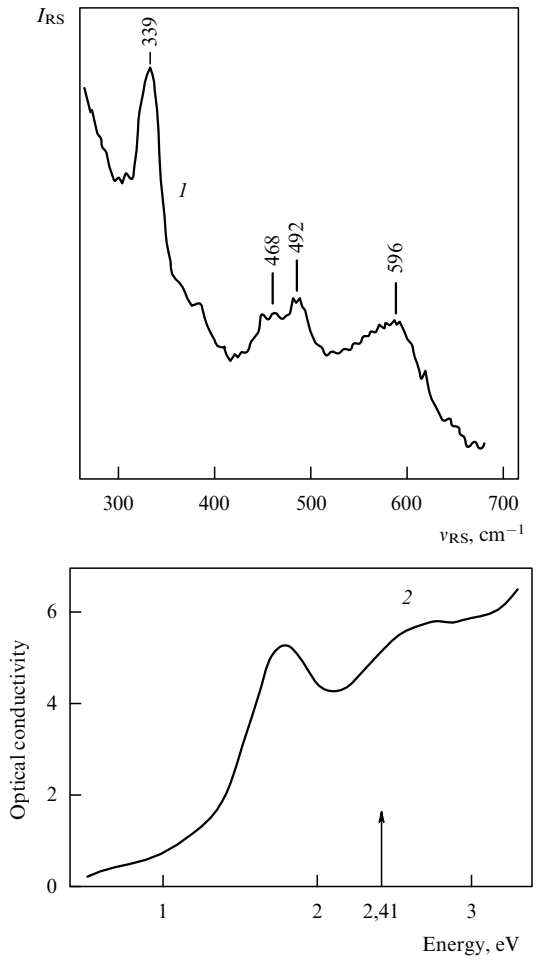

Figure 13. RS spectrum of a ceramic 1:2:3 sample excited by the 514.5 nm radiation of an argon laser (*1*). Curve (*2*) (energy dependence of photoconductivity of the same sample) illustrates resonance conditions [41].

Other results on this subject were obtained in Ref. [168], where attention is drawn to the fact that in a specific experimental geometry the RS spectrum exhibits a clear-cut peak at 2.5 eV (Fig. 14). Based on the earlier suggested model [169, 170], the authors of Ref. [168] appeal to the properties of the ground electron state formed by an odd combination of the ion orbitals of apical oxygen, which does not hybridize with the orbitals Cu(1) dy^2z^2 and $d_{3z^2}-r^2$ because of difference in parity and makes π bonds with other orbitals of Cu(1).

In summary, from the structural and spectroscopic standpoint, cuprates may be thought of as compounds which consist of two copper-oxygen subsystems — chains and layers. It is this point of view that is consistently developed in Refs [171–173]. In recent years such an approach was extended to some other properties of these materials [174].

6. Quantum beats in the physics of HTS

The first attempts of using this method for investigation of cuprates were preceded by a series of experiments with simpler, although not transparent, objects such as metals and semiconducting materials. Simultaneously, adequate

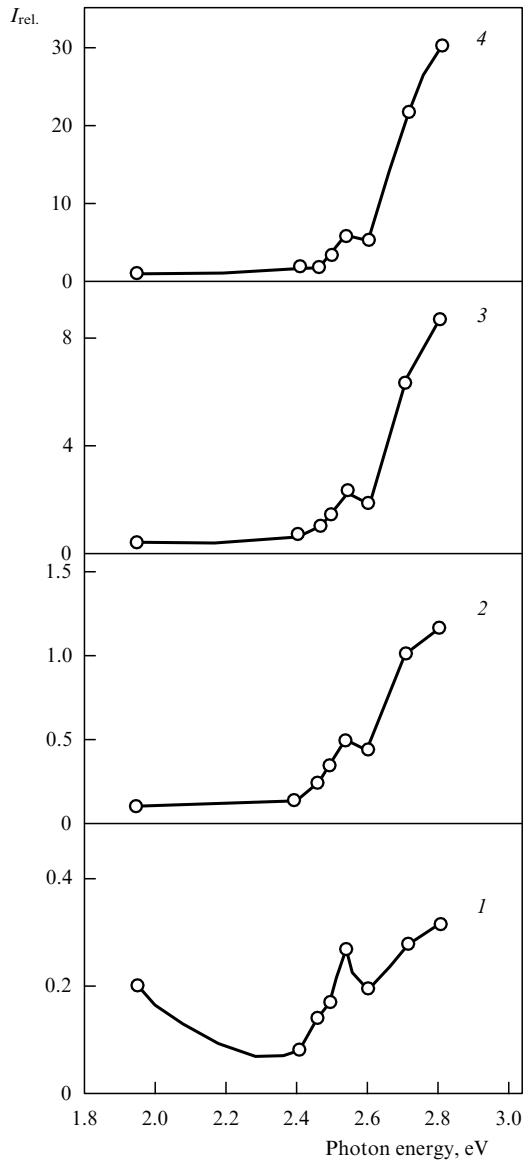

Figure 14. RS spectrum for full-symmetry phonons in a single crystal of $YBa_2Cu_3O_{7-x}$ for *zz*-polarisation: (*1–4*) 116, 150, 435 and 500 cm^{-1} phonons, respectively. A peak of unknown origin is seen at 2.5 eV [168].

theoretical concepts were developed. From our standpoint, particular attention should be given to the results obtained by Zeiger et al. [175].

Starting from the fact that the resonant RS spectra of metals, such as Sb, Bi and Te exhibit vibration modes of A_{1g} and E_g symmetry but only the first one in the form of quantum beats, the authors of [175] developed a theory in which the rates of the electron-excitation processes are taken into account in correlation with the relaxation of nuclei. It is assumed that under the action of an ultrashort (several femtoseconds) pumping pulse, the electron subsystem rapidly comes to a quasi-equilibrium state (in a time less than the relaxation time of vibrations). In other words, the electron transition takes place in a so short time interval that the motion of nuclei has no time to accommodate to a new equilibrium state.

In materials with vibration modes of A_{1g}-type symmetry, a quasi-equilibrium coordinate varies in the absence of structural rearrangement of a sample, which corresponds to the case when coherent vibrations occur about the initial point of equilibrium. From the mechanism proposed, an important conclusion is drawn that the generation of coherent vibrations is in general an exclusive property of highly symmetric modes and this is an explanation of the results obtained [175]. However, the reservation is made that the situation may be different if the system undergoes a phase transformation in the course of pumping.

Let us consider a purely methodical remark which could throw doubt on the validity of the experiments themselves. In our opinion, the proposed model may be applied to only simple molecular systems or low-dimensional solid-state structures (nanocrystals, clusters and localized states) in which during electron excitation the equilibrium nuclear spacing for the fully symmetric coordinates changes markedly and RS spectra are described near a resonance by the Franck – Condon mechanism. Otherwise, all the reasoning brought forward by the authors of the cited work breaks down.

Strange as it may seem, but in the case of HTS materials the situation is more favorable because of their specific morphology. On the other hand, the formation of a quantum beat spectrum may occur near the phase transition. It is these facts that give the chance to find these quantum beats for non-fully symmetric modes. A proper candidate for experiments of this sort might be the 210 cm^{-1} B_{2g} vibration mode of 1 : 2 : 3 cuprates, one of the most intense modes in the resonant RS spectrum for the *zx* polarization [54]. The results obtained might serve as a criterion for the adequacy of the model itself.

A theoretical treatment of quantum beats on the molecular scale has shown [176] that it is only possible with the violation of the adiabatic and Condon approximations. If this is also the case for solids, in particular cuprates, then it is of importance to take into account the specificity of apical-oxygen vibrations, namely, their nonadiabaticity. This may be formulated in other words: the strong nonadiabaticity of some vibrations in cuprates is favorable for the processes of formation of coherent modes which show up themselves in the form of a quantum-beat spectrum.

The extension of the above-mentioned method to HTS materials has many advantages. The primary advantage of this method is that it provides a possibility to obtain new independent information about all the characteristics of vibration modes in their dynamics, that is, in different phases of these modes on the real time scale. In particular, this offers promise for direct measurements of the time dependence of EPI.

Indirect data on the character of some processes in different systems induced by optical excitation were earlier derived from the band profiles of stationary RS spectra or IR spectra. However, in this case serious problems arose when one attempted to identify the true nature of the measured quantities. This refers, in particular, to the problem of separating the effects of dephasing of vibrations and their relaxation rate. Noteworthy also is a low sensitivity of the traditional methods in comparison with the direct quantum-beat method. There is yet another possibility to improve experimental techniques, namely, pumping with the use of rather long trains of light pulses, correlated in phase.

To the author's knowledge, the first attempt to study cuprates with the use of resonant impulsive-stimulated (ISRS) was made by Chwalek et al. [46]. The spectra were excited using the two-pulse technique and observed as

quantum beats at the edge of the transmission band of a 1:2:3 film with the stoichiometric index $x \approx 0.4$. By varying x, the compound could be obtained in both phases. In the normal state of the film, clearly defined oscillations at a frequency of 142 cm^{-1} were found. This frequency corresponds to a mode which belongs to the A_{1g} symmetry group and is therefore active in the usual RS spectra. When changing to the superconducting state of the film, this mode vanished from the ISRS spectrum, which appeared to contradict the above-mentioned theoretical conclusions [175].

Taking into consideration the resonant nature of the ISRS spectrum, Chwalek et al. [46] explained this effect by the specific selection rules for ISRS in highly absorbed media. However, with this approach, the fact of the activity of high-symmetry modes in the resonant ISRS spectra of not only highly absorbed metals and oxides [175], but also of the dielectric phase of the cuprate [46] were overlooked. It is now clear that the authors of this work [46] overlooked another trivial possibility to interpret the effect, appealing to the fact that the transition into a supeconducting state is accompanied by a sharp increase in absorption of pumping and probing pulses, which may in turn decrease the sensitivity of the apparatus on the whole.

That this is indeed the case was conclusively shown by Albrecht et al. [47]. To detect output signals (changes in the reflectivity of the films of composition $YBa_2Cu_3O_{7-x}$ with $x < 0.10$), new techniques and schemes were used. In this case the authors succeeded in detecting the values of $\Delta R/R_0$ with an accuracy of 10^{-7}, whereas the threshold sensitivity of previous measurements in earlier experiments [46] was less by two orders of magnitude.

It is appropriate to add some details to the above-described features of the experiment [47]. The films to be studied were fabricated using two methods: laser sputtering or passing a constant current through a sample. Crystalline $SrTiO_3$ was used as a substrate. In both cases the results of the investigation were the same. The films were thick enough (300 nm) for the unfavorable effect of interference to be eliminated. To avoid accidental errors, the experiments were performed on ten samples. The temperature was varied from 4 to 330 K. It was previously established that the increase in the film temperature due to pumping did not exceed 2 K. The film stoichiometry was controlled by X-ray diffraction and electron microscopy. Oscillating output signals were analyzed using the fast Fourier transform technique. The amplitude, width and dephasing of the modes with frequencies of 150 and 120 cm^{-1} were studied.

Some results of this work are illustrated in Figs 15 and 16. Figure 15 shows the behavior of reflected signals at temperatures above and below T_c. The insets present the operating portions of the spectra. As is seen, the inversion of the intensities of these modes occurs depending on the sample temperature. Simultaneously, there is observed a small shift of their frequencies. Using the literature data, both effects were interpreted on the basis of the temporal dependence of permittivity and the temperature dependence of the RS tensor. The shape of the corresponding vibrations was also taken into account.

In the context of this review, of particular interest is the temperature dependence of the output signal. As is seen from Fig. 16, the 150 cm^{-1} mode is characterized by $\Delta R/R_0$ values of about 5×10^{-6} when the film temperature changes from the highest temperature of $\sim$250 K down to 120 K. With further decreasing temperature, the value of $\Delta R/R_0$ slightly decreases, passing through a shallow minimum at a temperature of about 50 K. On the contrary, the 120 cm^{-1} mode is characterized by an extremely low value of the signal at high temperatures and a drastic increase of the signal near T_c.

Both the vibrations correspond to the motion of ions along the c axis of the 1:2:3 crystal. However, in the second

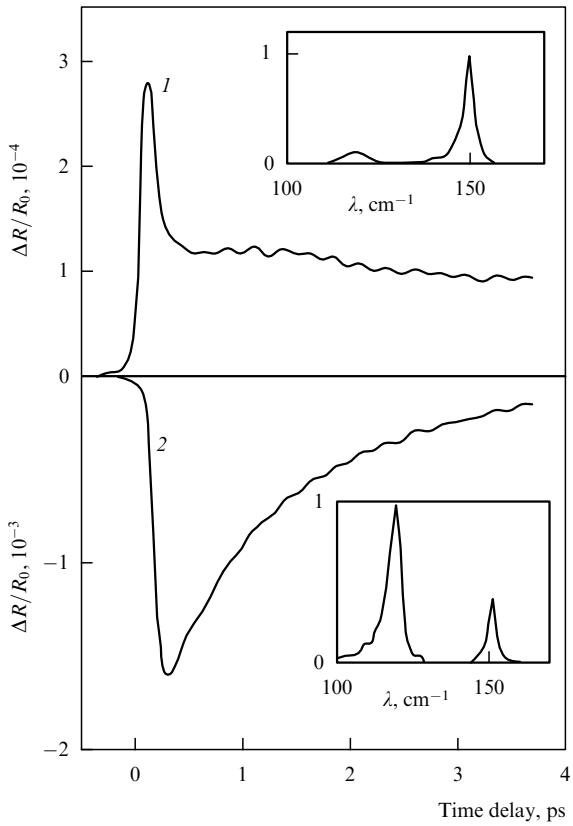

Figure 15. Time-delay dependence of the reflectivity of 1:2:3 films in the superconducting phase at temperatures of 300 K (*1*) and 40 K (*2*). In the insets: RS bands detected by the method of fast Fourier-transform spectroscopy [47].

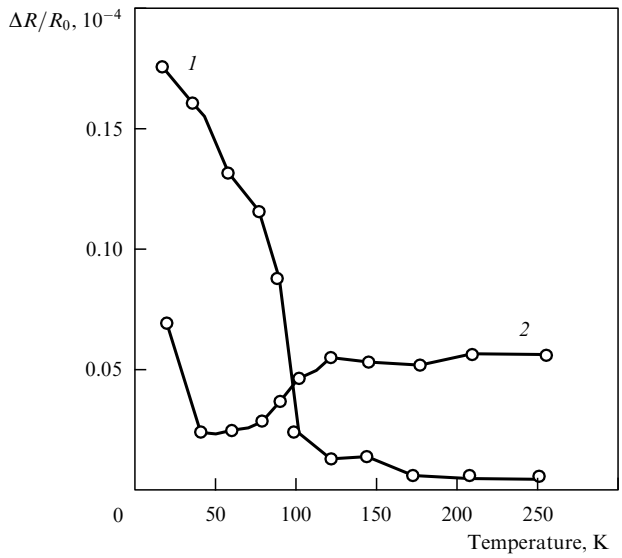

Figure 16. Temperature dependence of the photon-induced variations of reflectivity of 1:2:3 films in the superconducting phase. Measurements for the vibration modes of 120 cm^{-1} (*1*) and 150 cm^{-1} (*2*) [47].

case (120 cm^{-1}) barium ions are partially surrounded by apical oxygen atoms. Therefore, one is led to take into account the possible influence of the motion of barium ions on the process of charge transfer from chains to layers, which is enhanced by the phase uniformity of the excited waves. The even more drastic jump of the measured signal, resulting, as we assume, from a sharp increase in the number of carriers in conducting layers, might be expected for those fully symmetric modes with a frequency of about 500 cm^{-1} that are associated with the motion of the O(4) ions.

Thus, at the current stage of investigation it is difficult to make a definitive inference regarding the role of specific selection rules in the behavior of resonant ISRS for the superconducting phase of cuprates. This problem still remains urgent and there is no question that this line of investigation will be developed [177, 178].

7. Advisability, prospects, and ways of using the new methods of RS spectroscopy

In this review, attention was drawn time and again to many facts indicative of the cluster structure of some cuprates. This problem was further developed in a series of works on systems capable of changing into a glass state. For example, Kim et al. [179] were the first to succeed in observing phase separation when obtaining glasses by quenching of the melt in the Bi – Sr – Ca – Cu – O system, which was accompanied by precipitation of crystals of a superconducting phase with dimensions of 5 – 10 nm. (X-ray diffraction, differential thermal analysis and electron microscopy were used in these experiments.) More recently such experiments were extended to the same system with additions of Pb [180]. This facts put in the forefront the problem of adaptation the method of RS spectroscopy to new conditions.

For this purpose, investigations of the low-frequency region of acoustic vibrations (below about 100 cm^{-1}) are appropriate [181]. Their description is based on the model of a continuous elastic body. As applied to the case of a spherical particle, it was shown that acoustic modes fall into spheroidal (s) and torsional (T) modes with frequencies depending on the longitudinal (v_l) and transverse (v_t) velocity of sound, and can be written in the following form:

$$\omega_{l,n}^{s,T} = \eta_{l,n}^{s,T} \frac{v_t}{2\pi a c} , \tag{7.1}$$

where a is the particle radius, η are numerical coefficients determined by the ratio v_t/v_l, l is the angular momentum, and $n = 1, 2, 3, \ldots$ is the vibration number. Admissible values of l determine the finite number of degrees of freedom. It turns out that in an RS spectrum only the modes with $l = 0$ and 2 are active and only a few of them exhibit marked intensity. It is important that the study of the low-frequency acoustic branch of the spectrum allows one to make quantitative estimates of the degree of contact of particles with the surrounding matrix, that is, eventually to judge to what degree their surface is free [182].

Consideration of a solid as an elastic medium in connection with the possible role of its optical modes in the phenomenon of superconductivity was used recently by Tamura [183].

It has already been mentioned that quantum-beat spectroscopy is also a method of good promise for studies of low-frequency acoustic modes despite the fact that its theoretical basis is not completed.

Without exaggeration, the author is prone to advocate that the method of resonant hyper-Raman scattering (RHRS) would be of great importance in connection with the problem of HTS.

Optimism comes from the fact that the process of HRS unlike the usual RS, involves three rather than two photons and this may result in a radical change of selection rules for the appropriate quantum transitions. As a result, not only a number of vibration modes forbidden in the usual RS become activated, but, under certain conditions, also modes which are active neither in RS spectra nor in IR absorption ('silent modes') [136]. Of interest, for example, is the use of this method for the investigation of the above-mentioned effect of photogeneration of carriers in chains and conducting layers. The RHRS selection rules are favorable for such an investigation.

From the experimental standpoint, it is of great importance that HRS, being a three-photon process, is characterized by an extremely low cross section. This limits the possibilities of detection of the HRS spectra in cuprates even under optical-resonance conditions.

Since the possibilities of investigation of not only the HRS, but also the usual RS spectra are strongly dependent on considerable absorption losses for incident and scattered radiation in cuprates, the author believes that the following new experiment is possible and adequate to the situation discussed. It is based on well-known investigations of quantum size effects in nanocrystals of semiconductors, like CdS, which are introduced into glass matrices. In these experiments samples remain transparent in the optical region and, according to theory, their absorption edge exhibits a sharp shift to higher frequencies [184].

Thus, the idea proposed consists in producing highly dilute solid solutions of superconducting materials, which makes it possible to optimize absorption in a trivial way and under favorable conditions, through the size-effect-related shift of its boundary as well. To solve this problem, a proper matrix and technology of its use must be chosen. It should also be noted that in this case it is, in principle, possible to obtain an increase in T_c [185].

The data presented in the literature testify that on the current level of technology the difficulties arising from the extremely low cross sections of the process of HRS can be overcome. In this connection we refer to the recent publication [186] where the results of an investigation of CdS nanocrystals were reported. Resonance spectra were excited by the pulsed radiation of a frequency-controlled composite-rod laser (Ti : sapphire, 1.35 – 1.72 eV). The peak power, pulse width, and repetition rate were 1 kW, 30 ns and 3 kHz, respectively. A multichannel detector was used for registration of output signals. A simple monochromator with a resolution of 25 cm^{-1} was used as a spectral device. Similar apparatus was used more recently in studies of $CdBr_2$ nanocrystals [187]. It is curious that the usual resonant RS spectra from these objects have not as yet been described. Quantum-beat spectra from these nanocrystals were also obtained.

It is hardly probable that the experimental conditions in the cited works were optimal. In recent years considerable progress has been made in the creation of new types of lasers of this sort. For example, a laser was described producing terawatt pulses with a width of 45 fs and a repetition rate of 10 Hz. Since with such narrow pulses the probability of disruption of a sample is small, it is not inconceivable that

on the basis of their use, optimal conditions for RHRS experiments will be achieved and time-resolved measurements will be possible.

According to the literature, of great importance for the physics of HTS are the anharmonic properties of the real vibration modes of cuprates. Their strong interaction is likely to be a result of this anharmonicity, and this manifests itself in RS spectra. The case in point is the natural anharmonicity. However, it may also be induced by an intense electromagnetic field in the process of single-pulse SRS. This technique provides a possibility to achieve a considerable degree of occupation of excited vibrational levels and, in the limit, transfer half of the scattering particles to the first excited state, eventually resulting in a high concentration of anharmonic oscillators.

It is amply clear that during the application of a pumping pulse, the conditions under which the process of HTS goes on are radically changed, because of a sharp increase in the carrier concentration in particular. This in turn involves a change of the character of phonon spectra.

The difficulties of such experiments lie in the fact that intense light pulses can destroy samples, especially in the cases where the excitation of SRS is accomplished near or within the absorption bands. To minimize this unfavorable effect, very short pulses, for example, of a picosecond duration, should be used. In the case of wide RS bands, this offers an additional advantage because of reducing the threshold for generation. This is indeed the case with the RS spectra of cuprates.

Thus, the single-pulse SRS experiments in superconducting materials have in our opinion a clear physical meaning and, not inconceivable, are of pure utilitarian interest and considerable promise for their realization.

In contrast to the 'classical' SRS, nonthreshold SRS does not require the application of extremely intense pulses of radiation. Essentially, the method is as follows.

Let us suppose that two light pulses of essentially different intensity with frequencies ω_1 and ω_s and wave vectors $\mathbf{k}_1$ and $\mathbf{k}_s$ act on a sample. If they are superposed in time and space, coherent vibrations are excited in the sample, which form elastic waves with $\omega_0 = \omega_1 - \omega_s$, $\mathbf{k} = \mathbf{k}_1 - \mathbf{k}_s$, where ω_0 is the frequency of one of the active (in scattering) vibration modes. It is just this mode that contributes to the nonthreshold process of SRS. In this case, weak radiation of frequency ω_s is enhanced at the cost of radiation ω_1. This occurs owing to vibrational resonance. Such spectra may be excited, similarly to ISRS spectra, by a sufficiently long pulse train. Using a probing pulse with a time-controlled delay enables one to make kinetical measurements.

Nonthreshold SRS is noted for its high sensitivity and selectivity, which was demonstrated by Heritage and Allars [189], obtained a good spectrum from a monolayer of *p*-nitrobenzoic acid adsorbed on the surface of aluminum in the picosecond-excitation mode. In the literature, data also exist on the application of vibrational resonances observed in HRS spectra to studies of polaritons in molten quartz [190]. The extension of such experiments on cuprates holds much promise.

8. Conclusions

The effect of HTS, being one of the most resplendent discoveries in the field of physics in the last decade, immediately attracted attention of theorists and experimentalists who are able to use modern tools and methods for the study of the structure and various properties of solids. RS spectroscopy occupies a prominent place among these methods. Nevertheless, the problem of the unambiguous interpretation of experimental results has yet to be solved.

It has become quite evident that phonons play an important, if not predominant, role in the mechanism of HTS. This puts in the forefront the consideration of their peculiar properties, such as anharmonicity, adiabaticity, and others, which was demonstrated in numerous publications. It is also clear that such investigations must be conducted in the context of general concepts of the structure of substance and of the characteristic features of RS spectroscopy as a diagnostic method. This idea is at the basis of this review.

When discussing structural problems, worthy of notice is an approach based on the concept of localized pairs of valence electrons, which takes into account the donor and acceptor properties of the partners of the resulting chemical bonds. Using this concept and some additional grounds, it is possible to qualitatively interpret the behavior of some cuprates with a chain subsystem. In addition, this opens a direct way to comparisons and useful analogies with a number of complex organic compounds considered as model objects. Thus, the concept of charge-density waves is introduced into the theory of RS, which is important for the interpretation of results.

The conventional RS spectroscopy, which found wide application in the problem of HTS, was enriched over many years by various versions including those that made it possible to perform time-resolved measurements. A crucial significance have taken the quantum-beat method, which permits one to follow the course of processes on a real-time scale. Although at present only two works have been made on cuprates using this method, the considerable promise for its applications in the physics of HTS is difficult to overestimate. In particular, one would expect promising results in studies of the temporal characteristics of EPI.

Since cuprates by their nature tend to cluster formation, it is reasonable to extend the method of low-frequency acoustic RS spectroscopy to these compounds. It is not inconceivable that in this case the use of the quantum-beat method will make it possible to gain a sharp increase in sensitivity and radically eliminate the deleterious effects of background in the vicinity of the exciting line.

In the author's opinion, SRS experiments using high-power single-pulse radiation are worthy of notice. By this means it is possible to realize the situation of induced anharmonicity and, hence, strongly affect the overall process of HTS and the shape of phonon spectra during the pulse action.

Of considerable promise for the elucidation of the true nature of photon-induced HTS would be the technique of hyper-Raman scattering, which obeys peculiar selection rules and enables one to observe new vibration modes not found when using the usual RS (allowed, for example, only in IR spectra).

For implementation of this program, it is appropriate to give preference to very thin superconducting films with an island structure as the objects of investigation. Solid solutions of nanocrystals of superconducting materials introduced into glasslike or organic matrices offer an alternative to these films. This will require the development of new technologies.

The author is very grateful to V Maslov and A Baranov for critical reading of the manuscript and M Tsenter for her assistance in the design of the figures.

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