Electron-phonon interaction in high-temperature superconductors

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The results of experimental studies of the interaction between electrons and crystal lattice vibrations in high-temperature superconducting metal oxides are presented. Attention is directed mainly toward a critical analysis of the data obtained by means of tunneling spectroscopy.

"What we do is try to simplify our calculations, while in reality we know nothing..." *M. Voloshin* ("The Universe," 1923)

I. INTRODUCTION

At the present time it can be regarded as a wellestablished fact that in the metal-oxide semiconductors, as in ordinary metals, at temperatures below the critical temperature T_c the electrons are bound in pairs in an energy band whose width is on the order of the gap, so that the pairing probably has a singlet character.¹ However, the mechanism responsible for the origin of the attraction between the electrons has still not been identified.² Where does it come from? Is it an electron-phonon interaction or is it a fundamentally new process, e.g., an interaction between the electrons and spin or charge fluctuations?

The theoretical aspects of the problem of determining the superconductivity mechanism in metal-oxide compounds have already been the subject of a number of review articles, of which the most recent³ presents convincing arguments in favor of the electron-phonon interaction (EPI). We will therefore deliberately restrict ourselves to the question of how the EPI manifests itself in the experimental properties.

The most comprehensive information about the oscillation spectrum of the crystal lattice, the EPI function $\alpha^2 F(\omega)$, and the strength of the electron-phonon bond comes from the electron tunneling technique.^{4,5} Hence we will mainly review work on EPI tunneling spectroscopy in metal oxides, leaving a survey of the results of other experimental techniques which provide information about the electron-phonon interaction for Sec. 3. It seems to us that this compressed and of course incomplete summary of the data together with an outline of the related theoretical predictions will be useful for understanding all the complexity of this problem.

2. TUNNELING SPECTROSCOPY OF PHONON EXCITATIONS

As is well known, studies of the current-voltage characteristics of layered metal-insulator-metal tunneling structures were crucial in helping to provide a unique determination of the phonon pairing mechanism for most conventional superconductors.^{4,5} However, there the interest was mainly in nontransition metals. For the transition metals tunneling spectroscopy encountered a difficulty in principle, associated with the relatively short mean free path $l_{\rm ph}$ for electronic excitation when the energy $\omega = E - E_{\rm F}$ is of the order of the phonon energy (see, e.g., Svistunov and Belogolovskii⁴).

Let us consider this problem in more detail for the high-temperature superconductor La-Sr-Cu-O. Taking the Fermi velocity to be $v_F = 8 \cdot 10^6$ cm/s (Ref. 6), the characteristic phonon frequency to be $\bar{\omega} = 40$ meV, and setting Im $Z_N(\bar{\omega}) = 1$ (where Z_N is the renormalization function) in the formula $l_{\rm ph}(\omega) = (\hbar v_F/2\omega) \text{Im}Z(\omega)$ yields^{4,5} $l_{\rm ph}(\bar{\omega}) \approx 10\text{--}20$ Å, which agrees with the numerical value⁶ for the coherence length ξ_0 in the copper-oxide plane, i.e., with the characteristic distance over which the superconductivity order parameter varies where the S and N phases come in contact.

The latter fact implies that for metal oxides the probing depth is limited to distances of order ξ_0 , and even a slight reduction in the superconducting properties of the sample surface drastically changes the tunneling properties. In particular, there is a sharp drop in the amplitude of singularities in the differential conductivity, proportional to $Re(\Delta^2(\omega)/\omega^2)$ (Refs. 4, 5), as a result of which it is extremely difficult to detect the nonlinearities which correspond to phonons or other excitations responsible for electron pairing in the tunneling conductivity of systems with HTSC. Nonetheless, a considerable number of papers have already been published in which the nonlinearities in the tunneling properties of superconducting metal oxides are interpreted as a manifestation of oscillations in their crystal lattices.

While completing the work for this review article we received from K. Kitazawa a very comprehensive and interesting preprint,⁹⁶ in which attention is directed at the tunneling problem in HTSCs.

2.1. The La-Sr-Cu-O system

The appearance of electron-phonon interaction effects in the tunneling spectra of new materials having a high superconductivity transition temperature was the subject of Refs. 7–9, in which the electrical properties of point tunnel junctions made from lanthanum ceramic were studied (Fig. 1). Subsequently a similar structure [for



FIG. 1. Differential conductivity (dI/dV)(V) and the second derivative $(d^2I/dV^2)(V)$ of a junction formed by applying a microscopic indium drop to the surface of a lanthanum-strontium ceramic; here T=2.7 K (Ref. 8). The arrows indicate the locations of the phonon peaks.

 $V > (\Delta_{LSCO} + \Delta_{injector})/e]$ was detected also in the tunneling properties of a junction made from a niobium needle and one of the two phases of the single-crystal $La_{2-x}Sr_xCuO_{4-y}$ with $T_c = 12-13$ K (Refs. 10, 11). The relatively low superconducting transition temperature permitted the temperature dependence of these properties to be studied in detail: as T was reduced they shifted following the behavior of the sum of the gaps $(\Delta_{LSCO} + \Delta_{Nb})$; they remained after the transition of niobium to the normal state and vanished at $T = T_c$. This last fact implies that the structure cannot be the result of inelastic scattering of electrons on phonons in the barrier, since in this case it would not have disappeared in the normal state.

A detailed comparison of the behavior of the phonon density of states $F(\omega)$ and the location of the principal maxima and minima in the second derivative $(-dI^2/dV^2)(V)$ of the tunneling current with respect to the voltage for point junctions of an aluminum injector with the polycrystalline compound $La_{1.85}Sr_{0.15}CuO_4$ was carried out by Elkino.¹² Figure 2 shows their very convincing agreement; several additional maxima in the $(-dI^2/dV^2)(V)$ curve (in particular at 23 and 36 meV), which are missing in the neutron $F(\omega)$, according to Ref. 12 are associated with the singularities in the square $\alpha^2(\omega)$ of the EPI matrix element, or else with modification of the phonon spectrum of the HTSC material in the region near the surface. It should be emphasized that these irregularities in the tunneling curves cannot be caused by inelastic processes, since they must give rise to minima in $(-dI^2/dV^2)(V)$ at characteristic voltages corresponding to the phonon energies, and not to maxima as observed in Ref. 12. In order to identify these features, Elkino¹² performed a quantitative analysis of the correlations between the locations of the peaks in $(-dI^2/dV^2)(V)$ (the x coordinate) and the maxima of $F(\omega)$ (v coordinate). The method of least squares was used to determine the coefficients a and Δ in the relation $y = ax + \Delta$, which were found to be $a=1, \Delta=7$ meV. The value a=1 implies that these



FIG. 2. Second derivative $(-d^2I/dV^2)(V)$ of the tunneling current with respect to the voltage for two point junctions with an aluminum injector and polycrystalline La_{1,83}Sr_{0.15}CuO₄(T=4.2 K) (a) and the phonon density of states of this compound (b) (Ref. 12).



FIG. 3. Second derivatives $(d^2I/dV^2)(V)$ of the tunneling current with respect to the voltage for a junction formed by depositing a lead injector on a freshly cleaved surface of yttrium-barium ceramic (the solid trace is experimental and the broken trace is calculated) (a) (Ref. 13); phonon density of states of this compound (b) (Ref. 14).

features are in complete agreement, and the result $\Delta = 7$ meV yields the magnitude of the energy gap of the metal oxide in question.

2.2. The R-Ba-Cu-O system

Figure 3 (Ref. 13) shows the second derivative $(-dI^2/dV^2)(V)$ of the tunneling current with respect to the voltage (solid trace) for a junction between a lead film and an yttrium ceramic. Here also is shown the phonon density of states $F(\omega)$ found by Rhyne *et al.*¹⁴ for yttriumbarium metal oxide and the curve of $(-dI^2/dV^2)_{\text{theor}}(V)$ calculated from it (broken trace). As can be seen from Fig. 3, the minima of $(-dI^2/dV^2)(V)$ can be directly compared with the peaks of its vibrational spectrum. The appropriate quantitative analysis¹⁵ confirms that they are proportional to one another with a coefficient equal to unity and with a shift which is determined from tunneling theory⁵ by the magnitude of the YBCO energy gap (in this case for various samples it is equal to $\Delta_{\rm YBCO} = 14-19$ meV).¹⁵

Gurvitch *et al.*^{16,17} concluded similarly that the gap at ± 49 meV, reliably reproduced in the tunneling conductivity of the structures produced by sputtering a lead layer onto a chemically etched yttrium-barium cuprate surface, is of phonon origin. The peaks in the tunneling curves for Y-Ba-Cu-O given in Ref. 18, and also for the similar compounds of Sm-Ba-Cu-O (Ref. 19) and Eu-Ba-Cu-O (Ref. 10) are connected with the manifestation of the vibrational spectrum.

2.3. The Bi-Sr-Ca-Cu-O system

There is a number of papers in which it is asserted that phonon peaks have been observed in the tunneling curves of bismuth metal oxides. As an example, Fig. 4 shows the tunnel spectra of a point junction made from a tungsten point and a $Bi_2Sr_2CaCu_2O_{8+x}$ single crystal.²¹ In the first derivative (dI/dV)(V) at voltages greater than the maximum of the gap ($V \approx 22 \text{ mV}$) up to the peak in the region of 80 mV a jagged structure is observed which is symmetric about zero voltage. In the second derivative $(d^2 I/dV^2)(V)$ for positive bias it is converted into at least four separate peaks, corresponding to the stepwise increase in the differential conductivity [it should be emphasized that we are concerned here with the maxima in $(d^2I/dV^2)(V)$, and not in $(-dI^2/dV^2)(V)$ as was the case above]. In the opinion of Koltun et al.,²¹ this implies that in this case there are effects related to the opening of new tunneling channels at these voltages, of which the most probable process is inelastic tunneling involving barrier phonons (it is assumed that the tunnel barrier is made of a poorly conducting surface layer of bismuth metal oxide). The values of the phonon energy found from these results agree fairly well with the calculated oscillation frequencies for individual atoms in an elementary cell of this compound (this agreement was achieved in the case of eight out of nine of the observed peaks).

Contrary to the assertion made in Ref. 21, the authors of Refs. 22, 23, and 86 assumed that the nonlinearities in



FIG. 4. First (dI/dV)(V) and second $(d^2I/dV^2)(V)$ derivatives of the tunneling current with respect to voltage for a point junction between a tungsten point and a Bi₂Sr₂CaCu₂O_{8+x} single crystal. The arrows indicate the values of the oscillation frequency for the individual atoms in an elementary cell of this compound.²¹

the tunneling curves which they observed for the bismuth superconductor of the same composition are caused by elastic (and not inelastic) tunneling processes and reflect the structure of the energy spectrum of the HTSC compound.

A series of papers by Japanese workers^{24-26,75,90} is devoted to the phonon peaks in the tunneling characteristics of bismuth metal oxide. Tunneling junctions were fabricated by mechanically compressing a Bi₂Sr₂CaCu₂O₈ single crystal with small inclusions of (Bi2212) Bi₂Sr₂Ca₂Cu₃O₁₀ (Bi2223), and also a GaAs single crystal doped with Zn (similar junctions made from CaAs doped with Pb had a purely tunnel nature, as shown by the observation of the lead peaks in the measured phonon curves). Electron tunneling occurred both perpendicular to the c axis, i.e., in the (001) plane, and parallel to it. The measured value of the gap in the former case was 22 meV (Ref. 24), and in the latter case for some curves it was 21 meV and for others 32 meV (Ref. 26); (the latter value was attributed to the Bi2223 phase, and the Bi2212 gap was assumed to be essentially isotropic and approximately equal to 22 meV). Comparison of the peak locations for voltages up to 200 mV with the data obtained from Raman scattering demonstrated, in the opinion of the authors, that they are of phonon origin. Moreover, even multiphonon peaks were observed: for characteristics with $2\Delta = 44$ meV they were caused by two-phonon processes and with $2\Delta = 64$ meV by three-phonon processes²⁶ (multiphonon peaks were not present in the curves for the compound $Bi_2Sr_{1.6}La_{0.4}CuO_{\nu}$, which is analogous to Bi2201).⁷⁵ The authors of Ref. 25 believe that this means that multiphonon exchange between electrons in the HTSC compounds plays an important role. This exchange is responsible for raising the critical temperature; according to Ref. 25 it involves phonons belonging to the CuO_2 layers. In this case the familiar correlation between the value of T_c and the number of CuO_2 planes in an elementary cell becomes understandable.

This correlation appears most clearly in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ compounds (the magnitude of *n* corresponds to the number of CuO₂ planes between the layers of Bi_2O_2): for n=1 (Bi2201) we have $T_c=20$ K, for n=2 (Bi2212) we have $T_c=80$ K and for n=3 (Bi2223) we have $T_c=110$ K (Ref. 27).

In fact, if the tunneling characteristics of multiphonon structures are not seen in lanthanum-strontium metal oxides containing one copper-oxygen plane (see, e.g., Ref. 10), then in compounds with two Bi2212 layers twophonon peaks appear [Miyakawa *et al.*²⁶ also relate to them the peak at 100 mV in the tunneling properties of Eu-Ba-Cu-O (Ref. 10)] and with three layers (in particular, for Bi2223) three-phonon peaks appear. These arguments support the model of multiphonon exchange between electrons in such metal oxides and imply that further tunneling experiments in this direction are necessary.

2.4. The Ba-K-Bi-O system

The most important results in the spectroscopy of phonon excitations were obtained for the Ba_{1-r}K_rBiO₃ compound,²⁸⁻³⁰ which is the first superconducting metal oxide that does not contain copper ions. It has a simple cubic structure but has a fairly high (relative to the usual semiconductors) critical temperature $T_c = 30$ K (x =0.375). These objects are polycrystalline specimens for which the barrier is the naturally occurring insulating laver on the surface. In Refs. 29 and 30 layers of indium and tin deposited from above acted as the injector. Reproducible peaks were observed in the second derivative $(dI^2/dV^2)(V)$, which agreed both in position and in shape with the peaks known from neutron measurements of the phonon density of states (furthermore, there is a cutoff near 80 meV, which agrees with the boundary of the phonon spectrum). The total disappearance of these peaks for $T > T_c$ (rather than weakening as a function of temperature) implies that they are related to the superconducting state. This fact, and also the fact²⁹ that for the same phonon energies minima (and not peaks) are observed in $(dI^2/dV^2)(V)$ allows us to reject unequivocally the effect of inelastic tunneling as the source of the above anomalies.

This last argument also applies to the compound $Bi_2Sr_2CaCu_2O_8$ discussed above,²⁴ which also has insulating phases at the surface, so that inelastic tunneling in which phonons take part in the barrier is excluded in this case.

Further studies of the compound $Ba_{1-x}K_xBiO_3$ were carried out using point junctions made from a gold point.²⁸



FIG. 5. Derivative $(d\sigma^-/dV)(V)$ (after subtracting out the background) of the odd part of the tunneling conductivity of a Pb/YBCO film junction (a) and the shape of the spectral function $\alpha^2 F(\omega)$ reconstructed from it (b, solid trace). The broken trace in b is the phonon density of states for an yttrium-barium metal oxide.¹³

*2.6. Reconstruction of the electron-phonon interaction function

Let us comment briefly first on the attempt to reproduce the shape of the electron-phonon interaction function $\alpha^2 F(\omega)$ for nonsuperconducting yttrium-barium metal oxide.²⁰ As is well known, the phonon spectrum is reflected in the tunneling properties not only of the superconducting but also of the normal metal, in the form of both elastic and inelastic channels.⁹¹ The addition to the elastic component resulting from the transparency of the barrier as a function of the energy of the tunneling electron is odd in the voltage and proportional to the real part of the renormalization function describing the change in the electron energy due to its interaction with the lattice vibrations. In Refs. 20 the effect of the odd 13. nart $\sigma^{-}(V) = (\sigma(V) - \sigma(-V))/2$ of the differential conductivity of a Pb/YBCO film tunnel junction on the occurrence of maxima related to the energy gap of yttriumbarium metal oxide was identified. Figure 5 shows the derivative $d\sigma^{-}/dV$ (after subtracting out the background) and the (unnormalized) function $\alpha^2 F(\omega)$ of the elementary excitations reconstructed from it using the technique of Ref. 91. These excitations make up the self-energy correction to the electron energy (Fig. 5b, solid trace). In terms of the location of the main peaks this function agrees fairly well with the phonon density of states of the yttriumbarium compound known from neutron measurements. According to Ref. 13 this is yet another confirmation of the role of the electron-phonon interaction. Vedeneev *et al.*^{22,23} have reported finding the shape of

Vedeneev et al.^{22,23} have reported finding the shape of the spectral dependence of the electron-phonon interaction for two types of superconducting bismuth-containing metal oxides [the amplitude values of $\alpha^2 F(\omega)$ and the constants λ and μ^* were not given]. The Bi-Sr-Ca-Cu-O single crystals which were studied contain two phases with $T_c = 65$ K and 23 K [these values were determined from the temperature dependence $\Delta(T)$ of the gap]. The experiments were



FIG. 6. The function $\alpha^2 F(\omega)$ of the superconducting BiSrCuCaO metal oxide with $T_c = 65$ K (trace 1) and 23 K (trace 2). Trace 3 (points) is the phonon density of states $F(\omega)$ for this compound.²²

carried out either with samples consisting almost entirely of a single high-temperature phase, or in single crystals containing only the low-temperature phase. On the whole, these traces are qualitatively similar to the phonon density of states $F(\omega)$ of the same material found from neutron measurements [as can be seen from Fig. 6, closer to the neutron curve of $F(\omega)$ in the case of the data for the low-temperature phase]. The difference between the two functions $\alpha^2 F(\omega)$ is mainly that in the case of the hightemperature phase $\alpha^2 F(\omega)$ is nonzero in a somewhat narrower range of ω , and furthermore there is no dip in the region of intermediate frequencies 40-60 meV. It is possible that this difference in the spectra is the reason for the increase in T_c in the high-temperature specimens.

A notable success of tunneling spectroscopy of superconducting metal-oxide compounds was the investigation in Ref. 28 of the Nd-Ca-Cu-O and Ba-K-Bi-O systems using the technique with modifications to include the effect of closeness⁵ [the results obtained in reconstructing $\alpha^2 F(\omega)$ for these metal oxides are shown in Fig. 7]. The compound $Nd_{2-r}Ce_{r}CuO_{4-v}$ is a typical representative of the metal oxides with electron conductivity. In Ref. 28 point junctions of crystalline Nd_{1.85}Ce_{0.15}CuO_{4-y} ($T_c \approx 23$ K) samples with a gold point were studied. For voltages near V=0 the tunneling properties exhibited marked gap features, and the ratio $\sigma_{\rm S}/\sigma_{\rm N}$ of the differential conductivities at zero voltage in the superconducting and normal states was equal to approximately 0.1 at T = 4.2 K, which is a fairly good result for such materials, although it is considerably greater than the value which should be obtained when only temperature spreading is taken into account. The same value $\Delta = 3.7 \pm 0.1$ meV and correspondingly, $2\Delta/(kT_c) = 3.9 \pm 0.4$, was found for the 15 transitions studied, and it was possible to reconcile the calculated and experimental values of the critical temperature for the superconducting transition. We present specific results for two samples with composition $\lambda = 0.9 \pm 0.1$, $\mu^* = 0.05 \pm 0.05$, $Nd_{1.85}Ce_{0.15}CuO_{4-y}$: $T_c^{\text{calc}} = 21$ K, $T_c^{\text{exp}} = 23$ K (Fig. 7a).



FIG. 7. The function $\alpha^2 F(\omega)$ for $Nd_{2-x}Ce_xCuO_{4-y}$ (a) and $Ba_{1-x}K_xBiO_3$ (b). The broken trace represents the phonon density of states $F(\omega)$ of $F(\omega) Nd_{2-x}Ce_xCuO_{4-y}$ and the points represent the function $G(\omega)$ obtained from neutron experiments for $Ba_{1-x}K_xBiO_3$; reflecting the basic behavior of the phonon spectrum.²⁸

In addition to this system, Huang et al.²⁸ used similar point junctions to study the compound $Ba_{1-r}K_rBiO_3$ (Fig. 7b). At T = 4.2 K almost ideal tunnel characteristics were obtained near the energy gap Δ with very small leakage currents $(\sigma_{\rm S}/\sigma_{\rm N}(V=0) < 0.01)$ at T=4.2 K and sharp spikes at $V = \pm \Delta/e$. Reconstruction of the electronphonon interaction function $\alpha^2 F(\omega)$ for the two samples with composition $Ba_{1-x}K_xBiO_3$ with $T_c = 24.5 \pm 3$ K (Ref. 28) yielded the results $\lambda = 1.2 \pm 0.2$, $\mu^{*} = 0.11 \pm 0.04$; the good agreement of $\alpha^2 F(\omega)$ with the neutron data, and also of the calculated and experimental values of $T_{\rm c}$ for this compound and for the electron superconductor $Nd_{2-x}Ce_{x}CuO_{4-y}$ according to Ref. 28, implies that the electron-phonon interaction is the dominant mechanism responsible for electron pairing in these materials. However, according to Huang et al.,²⁸ the possibility is not excluded that some other pairing mechanism also exists, whose magnitudes may be up to 25% of the phonon contribution.

Nevertheless, it would seem that this conclusion, which unambiguously supports the electron-phonon nature of superconductivity, at least in $Ba_{1-x}K_xBiO_3$, is confirmed by the results of the recent work of Dynes *et al.*⁷⁴ They performed extensive tunneling experiments in single crystals and thin films of four related compounds which were not layered, did not contain magnetic impurities, and hopefully involved the same superconductivity mechanism as the cuprates: $BaPb_{1-x}Bi_xO_3$ (BPBO), $Ba_{1-x}K_xBiO_3$

(BKBO), $BaPb_{1-x}Sb_xO_3$, and $BaPbO_3$. This technique, in which the "natural" barrier at the surface of these specimens was used as an insulator and the injectors were thin layers of In. Au. Pb. and Sn sputtered onto the surface or else a particle of indium injected into the oxide layer, as in Ref. 28 yielded ideal junctions with a conductivity ratio $\sigma_{\rm S}/\sigma_{\rm N}$ (V=0) less than 1%. For BPBO and BKBO compounds a pronounced structure was revealed in the tunneling properties at relatively low voltages (up to about 10 mV), which the authors unambiguously attributed to the binding of electrons to acoustic oscillations in the lattice. The value $\lambda = 1$ obtained for BPBO in the corresponding spectral range is clearly inadequate to account for $T_c = 11$ K. It can be conjectured that there is an additional effect from optical phonons whose contribution according to the estimates of Ref. 74 is about 1% to BPBO, and about 5% to BKBO. However, in BKBO it was not detected (apparently due to the high noise level⁷⁴), while in BPKO the structure observed at the level of tens of millivolts could scarcely be related to the electron-phonon interaction, since it was not reproduced from one junction to the next, was asymmetric in the voltage but symmetric in the current, was found in the range of voltages outside the range of the phonon spectrum, and increased as a function of the voltage. According to Ref. 74, all these facts, and also the small magnitude of λ inspire serious doubt as to whether the superconductivity in these bismuth oxides is entirely of electron-phonon origin.

Bulaevskii et al.¹⁰ presented electron-phonon interaction functions $\alpha^2 F(\omega)$ for two other metal-oxide com-Lounds and found the following values for the electronphonon coupling constant λ , the Coulomb pseudopotential μ^* , and the average energy $\langle \omega \rangle$: for LSCO they found $\lambda = 1.25, \mu^* = -0.16, \langle \omega \rangle = 175$ K; the calculated value of $T_{\rm c}$ was equal to 30 K, in contrast to the experimental value of 12-13 K; for the compound Eu-Ba-Cu-O they found $\lambda = 2.6, \mu^* = -0.1; \langle \omega \rangle = 560$ K and a calculated temperature $T_c = 196$ K. This work called attention to the peak at V = 100 mV, which is absent in the experimental curves for lanthanum metal oxides and is not observed in the phonon density of yttrium-barium cuprate (see Fig. 3b). Another attempt to reproduce the electron-phonon interaction function for bismuth-containing metal oxides was made in Ref. 95, in which tunnel junctions were studied which were fabricated using a point made of normal metal (Al or Ag) and the single crystal Bi₂Sr₂CaCu₂O₈. To process the experimental data they used a phenomenological model, which assumed that the differential conductivity rises sharply as a function of the voltage (on account of the normal component) and that the gap features of the superconducting state are smeared out due to the finite electron lifetime. The numerical values obtained in Ref. 95 for the electron-phonon interaction characteristics for two samples of the Bi₂Sr₂CaCu₂O₈ compounds were $T_c^{exp} = 80$ K, $\lambda = 2.5, \mu^* = -0.36, T_c^{calc} = 126$ K and $\lambda = 2.44, \mu^* = 0.27$, $T_{\rm c}^{\rm exp}=63$ K. The negative value of μ^* probably reflects contributions of tunnel and nontunnel nature that have not been taken into account: effects of lifetime, closeness and destruction of weak bonds, tunneling into the normal regions and into the region with reduced order parameter, leakage currents, etc.

We point out that the original experimental data must necessarily satisfy certain requirements, the principal of which is the sum rule (for more detail see Refs. 4, 93). The calculated and experimental values of the tunneling densities of state and of the critical temperature $T_{\rm c}$ must also agree (Ref. 92).

There is no possibility of drawing serious conclusions about the pairing mechanism on the basis of such "quantitative notions." Such situations have occurred previously. We recall the notorious "result" with $\mu^* < 0$ for niobium.⁹⁴ Only by including the closeness effect in the surface region and the low height of the potential barrier was it possible to obtain reliable numerical results for the function $\alpha^2 F(\omega)$ with $\mu^* > 0$ (Refs. 4, 5). All in all, oxide superconductors are very complicated materials, and proof of the reliability of the information about $\alpha^2 F(\omega)$ obtained in tunneling experiments is needed.

3. EXPERIMENTAL RESULTS ON THE ELECTRON-PHONON INTERACTION IN METAL OXIDES

3.1. The temperature dependence of the kinetic and thermodynamic properties in the superconducting state

At the present time there is a host of experimental facts which suggest that there is a significant difference in the temperature behavior of the dynamic characteristics of HTSC materials and ordinary superconductors. These become especially pronounced near the critical temperature $T_{\rm c}$ (see the discussion of this topic and the citations in Ref. 97). The best example of this sort is probably the absence of a sharp peak in the temperature dependence of the nuclear spin relaxation coefficient at a temperature somewhat below the critical value, one of the generally recognized proofs of the correctness of the BCS theory.³¹ The fact that this singularity is not observed in YBCO (Ref. 32) and other compounds³³ was the basis for the claim that the standard BCS theory is not applicable to these superconductors. Another characteristic example is the behavior of the London penetration depth, which according to Ref. 98 is more reminiscent of the results of the old phenomenological Casimir-Gorter model than the standard version of the BSC theory.

3.1.1. Density of the electron states. One possible way to overcome the discrepancy is to take into account the pair-disrupting factor which broadens the measured density of states and can even lead to a gapless state close to T_c (Ref. 34). It is found⁹⁷ that this factor may be inelastic scattering on thermal phonons, i.e., the usual electronphonon interaction, if it is strong enough and the temperatures $T < T_c$ are high enough. It has been shown^{97,99} in this case that the main role is played not by the "collapse" of the gap as the temperature approaches T_c , as occurs in the BCS theory with weak coupling, but by filling up of the low-energy states near the gap. The result is that the density of states is smeared out and, strictly speaking, there is no energy gap in the excitation spectrum at any nonzero temperatures (for more details see the review article of



FIG. 8. Effect of the temperature on the shape of the normalized density of states for superconducting bismuth metal oxide: $T=0.7T_c$ (long dashes), $T=0.8T_c$ (short dashes), and $T=0.9T_c$ (solid trace).⁹⁷

Ginzburg and Maksimov³). In the final analysis the presence of strong electron-phonon coupling leads to a significant relaxation time for the electron states, i.e., the inverse lifetime $\Gamma(\omega,T)$ which determines the shape of the normalized density of states of the superconductor is^{3,97}

$$N_{\rm S}(\omega) = \operatorname{Re} \frac{\omega + i\widetilde{\Gamma}(\omega, T)}{\left[(\omega + i\widetilde{\Gamma}(\omega, T))^2 - \widetilde{\Delta}^2(\omega, T)\right]^{1/2}}.$$
 (1)

In deriving this relation we have written the renormalized function $Z(\omega,T)$ in the Éliashberg equations in the form

$$Z(\omega,T) = \operatorname{Re} Z(\omega,T) + i\Gamma(\omega,T)\omega^{-1};$$

 $\Gamma(\omega,T) = \Gamma(\omega,T)/\text{Re } Z(\omega,T)$ determines here the strength of the pair-disruption effect; $\Delta(\omega,T) = \Delta(\omega,T)$ $\times Z(\omega,T)/\text{Re } Z(\omega,T)$ is the renormalized energy gap parameter, and the gap itself is determined by the relation $\Delta_0 = \Delta(\Delta_0, T=0)$. The effect of the unpairing factor $\widetilde{\Gamma}(\omega,T)$, which depends on the temperature and energy, on the density of states is clearly shown in Fig. 8, where the results of the calculation of Karakazov et al.⁹⁷ of the Éliashberg equations at T=0 are shown for one of the bismuth metal oxides, using the electron-phonon interaction function which was determined in Ref. 100. It is appropriate to note here that an expression like (1) for the density of states with the unpairing factor $\Gamma(\omega,T)$ is actively used in recent research describing the tunnel properties of high-temperature superconductors and their temperature dependence (see, in particular, Refs. 101 and 102 and the work cited therein). Moreover, from Fig. 8 it follows that because of the additional (with respect to the temperature) smearing of the density of states the location of the peak in $N_{\rm S}(\omega)$ changes fairly insignificantly as the temperature approaches T_c , which is also observed sometimes in tunneling experiments (see, e.g., Ref. 103).

3.1.2. The London penetration depth As shown in Refs. 97, 99, the behavior of the density of states described by Eq. (1) may be responsible for the unusual behavior of the thermodynamic and kinetic properties of the metaloxide semiconductors near T_c . This is clearly exhibited in the dependence on T of the London penetration depth λ_L ,



FIG. 9. Calculation of the temperature dependence of the function $\lambda_L^2(0)/\lambda_L^2(T)$ (here λ_L is the London depth of penetration) for superconducting bismuth metal oxide (stars), compared with the functions $1 - (T/T_c)^4$ (solid trace) and $1 - (T/T_c)^2$ (broken trace).⁹⁹

the square of which is inversely proportional to the density of states $n_{\rm S}(T)$ of the superconducting electrons. Filling up the superconducting gap with normal electrons as the temperature increases causes their density to be given not by the BCS formula, but rather by

$$n_{\rm N}(T) = 1 - n_{\rm S}(T) = (T/T_{\rm c})^4,$$
 (2)

which is well known from the two-fluid Casimir-Gorter model. Figure 9 displays the calculated results⁹⁹ of $\lambda_L^2(0)/\lambda_L^2(T)$ and compares them with the predictions of the BCS theory $\lambda_L^{-2}(T) \sim 1 - (T/T_c)^2$ and the two-fluid model $\lambda_L^{-2}(T) \sim 1 - (T/T_c)^4$.

3.1.3. Nuclear spin relaxation coefficient. We return again to the problem already noted above regarding the absence of a peak in the T dependence of the nuclear spin relaxation coefficient in HTSC materials for $T \lesssim T_c$. Allen and Rainer³⁵ performed the relevant calculations for model spectra of the electron-phonon interaction with different electron-phonon coupling constants from $\lambda = 0.805$ to $\lambda = 3.2$ (the latter value was chosen as an example for yttrium-barium compounds, since for $\mu^*=0.1$ it corresponds to $T_c = 90$ K). It was found that as λ increases the Hebel-Slichter peak is sharply weakened until it completely disappears in the case of HTSC materials (see Fig. 10, in which the experimental and calculated values for indium and yttrium-barium cuprates are shown). Thus, by itself the absence of this peak in the experimental curves does not prove that the superconducting state in metal oxide compounds is of an unusual nature. Furthermore, this fact can be completely explained using the standard theory of superconductivity if we include the strong interaction of the electrons with vibrations of the crystal lattice, and probably implies that an interaction like this is present in superconducting metal oxides.

3.1.4. Discontinuity in the specific heat at $T = T_c$. However, now we give an example of a different sort, related to the measurements of the discontinuity $\Delta C = \beta \gamma T_c$ in the specific heat at the superconducting transition point. Here γT is the electron contribution to the specific heat of



FIG. 10. Temperature dependence of the ratio of the nuclear spin relaxation rates in superconducting (T_{1S}^{-1}) and normal (T_{1N}^{-1}) states. The solid traces represent the results of calculations³⁵ using the electronphonon interaction function of indium (trace 1) and of lead for Pb_{0.9}Bi_{0.1} (trace 2 corresponds to $\lambda = 1.66$ and trace 3 to $\lambda = 3.2$ for the same spectral shape). The experimental data are circles for indium, squares for ⁶³Cu copper nuclei, and crosses for ¹⁷O oxygen nuclei in the CuO₂ planes of the Y-Ba-Cu-O system (taken from work cited in Ref. 35).

the normal metal at low temperatures (γ is the Sommerfeld constant) and β is a coefficient whose magnitude can be interpreted as an indirect measure of the strength of the electron-phonon coupling. Specifically, from Ref. 61 for an ordinary isotropic superconductor described by the Eliashberg equation we have $1.43 \le \beta \le 3.73$, where the lower limit corresponds to the weak-coupling case. However, recently values for the coefficient β have been obtained in HTSC materials that are of order 6 (see work cited in Ref. 62), which is larger than the maximum values for this quantity in the strong-coupling theory. After a number of unsuccessful attempts to interpret this fact (see, in particular, Ref. 62) Cohen and Renn⁶³ advanced a likely explanation. The point is that in the derivation of the expression for ΔC in the BCS theory the behavior of $\Delta(T)$ near $T < T_c$ plays an important role. However, as shown by Cohen and Renn,⁶³ the temperature dependence of the energy gap predicted by the BCS theory does not agree with the experimental $\Delta(T)$ curve. If, however, we substitute the measured form of $\Delta(T)$ in the expression for ΔC obtained in the weak-coupling theory, then the disagreement between theory and experiment is completely eliminated. Thus, in order to explain the values $\beta \ge 4$ there is no need to drag in ideas about very strong electron-phonon coupling. On the contrary, in the same experiments where the $\Delta(T)$ dependence was measured for the Bi₂Sr₂CaCu₂O₈, compound it was found that $2\Delta/kT_c \approx 3.3$, corresponding to very weak electron-phonon interactions. As shown in Ref. 63 cited above, this interaction suffices to describe the discontinuity in the specific heat for $T = T_c$.

3.2. Lattice properties close to the superconducting transition

3.2.1. Parameters of the crystal lattice. The behavior of the lattice properties, and in particular of the lattice



FIG. 11. Temperature variations of the lattice constants of $Ba_{0.7}K_{0.3}BiO_3$ (Ref. 39).

constants of the metal oxides near $T < T_c$, implies that the phonon mechanism has an important role in superconductivity. In this connection we refer to the work of Tody *et al.*,³⁷ in which it was found that the local structure of the Tl₂Ba₂CaCu₂O₄ compound changes in the transition to the superconducting state and to the work of Ono *et al.*³⁹ on observations of the anomalous behavior of the properties of the crystal lattice in the compounds Ba_{0.7}K_{0.3}BiO₃ at $T_c=29.2$ K, observed by means of x-ray scattering. As can be seen from Fig. 11, the parameter *a* in this metal oxide decreases gradually as the temperature falls until dropping sharply at $T=T_c$, while the parameter *c* first grows and then falls off in the same way at $T=T_c$ as does the parameter *a*.

3.2.2. Phonon spectrum. The effect of the electron subsystem on the lattice vibrations is exhibited directly also in the anomalous softening of the frequency of one of the optical phonons in HTSC compounds. Thus, e.g., in Zetterer et al.,⁴¹ (cf. the analogous data for yttrium-barium cuprate in Ref. 38 and the detailed discussion of this point in Ref. 40), in contrast to the usual behavior of the phonon frequencies, which rise smoothly as the material is cooled, the frequency of one of the infrared-active phonons in $Tl_2Ba_2Ca_2Cu_3O_{10}$ (300 cm⁻¹), first rose by 2% from room temperature to the critical temperature ($T_c = 112$ K) and then dropped discontinuously by 7%, after which it remained essentially unchanged until the lowest temperatures tested (Fig. 12). Note that in Ref. 42 the Raman spectrum line of the yttrium-barium compound at 333 cm^{-1} was softened by 9 cm⁻¹. The relation between the anomalous softening and the superconducting transition itself was confirmed by experiments on the effect of a magnetic field on this behavior.⁴³ The discontinuous softening of the lattice as the temperature was lowered near $T = T_c$ was observed in experiments on x-ray scattering and by measuring the reflection spectrum in the far-infrared region.⁴⁰ The anomalously sharp drop in the phonon frequencies near T_c is deduced from Mössbauer measurements performed with yttrium-barium samples in which copper ions were replaced with iron and tin (see, e.g., Ref.



FIG. 12. Temperature dependence of the frequency of an infrared-active phonon of $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Ref. 41).

44). On the whole the phonon spectrum of this compound remained essentially unchanged when it was cooled, and consequently the anomalous behavior of the lattice properties occurs only over a small region of momentum space. According to Refs. 45 and 46 for yttrium and bismuth metal oxides of different composition (from superconducting to semiconducting), this effect is unrelated to the structural transformations that take place, and is due to changes in the electron spectrum which are determined by the transition of these compounds to the superconducting state.

Generally speaking, the effect of the superconducting transition on phonons is slight, since the behavior associated with it occurs in a very narrow region of energies of order 2Δ near the Fermi energy. Consequently, the relative change in the oscillation frequencies of the crystal lattice must be less than $2\Delta/W$ (here W is the width of the electron band). In fact, it is even smaller because of various imperfections in the crystal: impurities, nonuniformity, etc. However, if the change in the lattice constants is consistent with this estimate, then, as can be seen from the remarks made above, some phonons still exist whose frequency undergoes shifts that are larger by almost an order of magnitude than those which should be expected based on the structural changes near T_c . A detailed analysis of the effect of the electron states which give rise to Cooper pairs on the optical phonons with wave vector $\mathbf{q}=0$ was carried out by Zeyher and Zwicknegel.⁴⁷ They found a universal relation for the change $\Delta \Sigma_i = \Delta \omega_i - i \Delta \gamma_i j$ in the characteristic energy of the *j*-th phonon mode with frequency ω_i and damping rate γ_i in the transition to the superconducting state, $\Delta \Sigma_i = \lambda_i \omega_i f(\omega_i/2\Delta)$, where λ_i is the electronphonon coupling constant for the *j*th mode and $f(\omega)$ is a universal function of the ratio $\bar{\omega}_i = \omega_i/2\Delta$ determined by the initial theoretical assumptions. All in all, the nature of the $f(\omega)$ dependence is clear from general considerations. The effect of changes in the electron spectrum on lattice vibrations with energies $\omega_i \ge 2\Delta$ when the energy gap Δ develops is small, and hence $f \approx 0$ for $\bar{\omega}_i > 1$. Near $\omega_i = 2\Delta$ a singularity develops in the polarization operator $\Pi(\omega)$, associated with the possibility of phonon states with $\omega_i > 2\Delta$ decaying. In the weak-coupling approximation (the BCS limit) this is an inverse square-root singularity for $\omega_i < 2\Delta$ and a discontinuity at $\omega_i = 2\Delta$ (in the strongcoupling approximation, and also when scattering from impurities is taken into account these singularities are smeared out). Below $\omega_i = 2\Delta$ the phonons are softened and



FIG. 13. Anomalous behavior of two optical photon frequencies in the systems $YBa_2Cu_3O_{7-x}$ (a) and $TmBa_2Cu_3O_{7-x}$ (b) (Ref. 48).

above $\omega_j = 2\Delta$ they are hardened, i.e., they are, in a manner of speaking, repelled from the region $\omega_j \approx 2\Delta$ (see Fig. 14).

This is precisely what was observed at the two phonon frequencies of 340 and 440 cm^{-1} near the superconducting transition, as measured in experiments on Raman scattering in ceramic specimens made from RBa₂Cu₃O_{7-x} (R =Eu,Sm,Tm,Y), in which the ¹⁶O oxygen ions in the yttrium samples were also replaced by their ¹⁸O isotopes (Ref. 48; see Fig. 13). The critical temperatures of these materials are the same, which means that the values of the energy gaps are very close (they must be exactly the same in the BCS theory, since the relation $2\Delta/T_c = 3.52$ holds, and differ very slightly in the strong coupling approximation due to the small variation in the frequencies averaged over the phonon spectrum). Consequently, a change in the composition of a metal oxide can bring about a shift in the unrenormalized phonon frequency by 2Δ , which confirms the predictions of the theory.⁴⁷ Figure 14, taken from Ref. 48, shows the frequency dependence thus obtained for the difference $\Delta \omega_i = \omega_i (T = 10 \text{ K}) - \omega_i (T = 90 \text{ K})$, and also the theoretical curve consistent with it calculated from the theory⁴⁷ using the parameters $2\Delta = 333$ cm⁻¹ $(2\Delta/k_{\rm B}T_c=5.2$ and $\lambda_i=0.02$). These values of the electron-phonon coupling constants for two specific modes agree with the calculated values determined in the same paper. An estimate of the total value of the constant λ assuming that the other lattice vibrations are coupled just as strongly to the electrons as the two phonons which were studied yields $\lambda = 0.6$ (Ref. 48), which is clearly inadequate to give $T_c = 92$ K and $2\Delta/T_c = 5.2$. In contrast to Ref. 48, in the experiments on Raman scattering⁷¹ YBa₂Cu₃O_{7-x} single crystals were studied. It was found that the change as the temperature decreased in all three of the modes studied (340, 435, and 500 cm^{-1}) agrees well with the predictions of the theory in Ref. 47 regarding the



FIG. 14. Relative change of the phonon frequencies in the RBa₂Cu₃O_{7-x} system at the transition to the superconducting state: the squares are experimental results and the solid trace is the theoretical dependence; here we have taken $\omega = \omega(T = 90 \text{ K})$, $\Delta \omega = \omega(T = 10 \text{ K}) - \omega(T = 90 \text{ K})$ (Ref. 48).

value of the ratio $2\Delta/k_B T_c = 5.9 \pm 0.3$. The anomalous behavior of the Raman-active phonon mode at 464 cm⁻¹ was observed also in the compound Bi₂CaSr₂Cu₂O₈.⁷² The theoretical predictions⁴⁷ are also confirmed by the results of Ref. 70, in which the temperature dependence of the linewidth was measured (10 K < T < 300 K) for the barium phonon mode at 115 cm⁻¹ in an yttrium-barium single crystal. The energy corresponding to it is much less than 2Δ , and hence for $T < T_c$ it is observed to fall sharply (by a factor of two when the temperature changes from 90 to 10 K) because no electron-hole pairs can be created.

Of course, the experiments described above cannot pretend to be a proof or disproof of the electron-phonon nature of superconductivity in metal oxides; they only indicate that there is an energy gap and that a coupling between the electrons and the lattice vibrations is present. Note, in addition, in this connection the work of McCarty et al.⁴⁹ in which the shape of the peak at 348 cm⁻¹ was analyzed in the Raman spectrum of $Ba_{1-x}K_xBiO_3$ in the normal (x=0.2) and superconducting (x=0.4) states, where it was shown that the corresponding optical phonon is strongly coupled to the electron continuum only for superconductors. We should also point out the work of Sugai,⁶⁹ who observed in the Raman scattering spectra of $La_{2-r}Sr_{r}CuO_{4}$ that as the strontium concentration increased forbidden phonon modes (infrared-active transverse optical phonons with the polarization vector parallel to the CuO_2 plane) began to appear. These features occur in metal oxides of the same composition for which superconductivity is observed, and are measured even at a temperature above the critical temperature. Sugai⁶⁹ relates this phenomenon to the presence of local distortions in the crystal lattice, which in turn are responsible for polaron effects. The fact that they manifest themselves only at strontium concentrations corresponding to the superconducting state implies according to Ref. 69 that there is a definite connection between these effects and the high- T_c mechanism, i.e., that the electron-phonon interaction plays an important role in the formation of the superconducting state. Ideas have been expressed (Ref. 66 and work cited therein) regarding the nonlinearities in the infrared

reflection spectrum, which are usually attributed to the energy gap of HTSC compounds (see, e.g., Ref. 68). The suggestion is that these are actually a manifestation of interaction with longitudinal optical phonons. These data uniquely imply that vibrations of the crystal lattice (directly or indirectly) are involved in the process by which the superconducting condensate forms in the metal oxides that have been studied.

In contrast to the data given above are the results obtained by measuring the temperature dependence of the phonon line shapes in a $La_{1.85}Sr_{0.15}CuO_4$ single crystal by means of inelastic neutron scattering, together with measurements of the effect of the superconducting transition on them.⁵⁰ The first experiments of this kind, carried out in 1973, in the ordinary superconductor Nb₃Sn (Ref. 51) showed that the lifetimes of certain acoustic phonons increase sharply as the temperature T is decreased and passes through $T_{\rm c}$ (the line width decreases by a factor of two). This applies to phonon states whose energy is less than 2Δ , and consequently their decay in the superconducting state by excitation of electron-phonon quasiparticles is not prevented. The same authors (together with other collaborators) performed similar studies in highquality single crystals of lanthanum-strontium metal oxide,⁵⁰ which yielded contradictory results: the line shapes for two acoustic phonons were practically identical at 50 and 5 K, i.e., no variations with temperature were observed (the phonon energy was in the range $\omega \approx 6.0-9.5$ meV and the line width was close to half of the maximum value $2\gamma \approx 0.25 - 0.5$ meV). Although the conclusion deduced from these data that the electron-phonon bond is weak in lanthanum samples is probably premature, the reason for the discrepancy with the optical measurements remains unclear. Possibly it is because acoustic phonons were studied in this case, or else because the directions of the crystal lattice was studied in which the magnitude of the energy gap due to anisotropy is relatively small.

3.2.3. Thermal conductivity. Measurements of the temperature dependence of the thermal conductivity $\varkappa(T)$ yield detailed information about the thermal transport processes in these specimens, the electron and phonon contributions, scattering of quasiparticles by one another and by defects, and about the structure of the material as a whole. Although analysis of these data even for ordinary superconductors is very complicated due to a large number of factors that affect the thermal processes in them, the overall picture at the present time seems fairly clear.⁵⁶ In the normal state for ordinary metals the electron thermal conductivity is considerably greater than that due to phonons. which contribute only a few percent to the total value of κ . However, the transition to the superconducting state drastically changes the ratio of these contributions, since, on the one hand, electrons that have condensed into pairs do not participate in heat transport (the electron thermal conductivity x_e decreases) and, on the other hand, they do not scatter phonons (the phonon contribution x_{ph} rises). The ratio of κ_e to κ_{ph} determines the behavior of the total dependence of $x = x_e + x_{ph}$ on T near T_c . In the majority of cases (pure conventional superconductors and a large frac-



FIG. 15. Temperature dependence of the thermal conductivity for $YBa_2Cu_3O_{7-x}$ in the semiconducting state $(x\approx2)$; the experiment is the chain curve and the theoretical values shown by trace *I* are calculated for $\gamma=0$) and the superconducting state $(x\approx0)$; the experiment is the dashed line and the theoretical curve *2* is calculated for $\gamma=80$).⁵⁹ The parameter γ is proportional to the contribution of the acoustic phonons to the electron-phonon coupling constant λ .

tion of alloys) a sharp decrease in x is observed in the transition to the superconducting stage. In some alloys which are so disordered that x_e is small, a rise in the thermal conductivity over its normal value in the transition to superconductivity can be observed (as noted above, the main reason for this behavior is the decrease in the phonon-electron scattering for $T < T_c$).

The behavior of the thermal conductivity in hightemperature superconductors is even more complicated and obscure. Several review articles^{57,58,67} have been devoted to this topic; they describe the situation fairly accurately as of the time they were written. Below we present only the main conclusions of this work. All in all, the metal-oxide cuprates are characterized by an unexpectedly large phonon contribution to the heat transport, which reaches 60% of the total thermal conductivity of the sample in single crystals and 90% in ceramics. The relatively small value of the electron thermal conductivity is due to the low carrier concentration, and also their scattering by defects (in particular, in polycrystals). The dominant role of phonons in the thermal transport process causes \varkappa to increase at temperatures below the critical temperatures, with a maximum in the vicinity of $T_c/2$ due to the abrupt increase in the phonon mean free path caused by the formation of the superconducting condensate (as an example, see Fig. 15, in which experimental data for superconducting and semiconducting $YBa_2Cu_3O_{7-x}$ are compared). The magnitude of the maximum was found to depend strongly on the quality of the sample, i.e., on the ratio of the phonon scattering by current carriers and by other sources (primarily lattice defects): in some metal oxides the maximum was barely discernible, while in others it was almost twice as large as $\kappa(T_c)$. In Ref. 59 the experimental data for polycrystalline yttrium-barium samples were adjusted below the corresponding theoretical $\kappa(T)$ curves for a superconductor by including additional processes for scattering of phonons by inhomogeneities (see Fig. 15). Except for the temperature range in the immediate vicinity of $T = T_c$, good agreement between theory and experiment

was obtained and the value of the electron-phonon coupling constant corresponding to the contribution of the longitudinal acoustic phonons was estimated to be $\lambda \approx 0.5$. The use of this technique to process the data on the temperature dependence of the thermal conductivity of YBa₂Cu₃O_{7-x} single crystals yields a value $\lambda = 0.1$ for the constant, which implies that the electrons are weakly coupled to the acoustic phonons.⁷³ Thus, measurements of the thermal conductivity of high-temperature superconductors unambiguously implies that there is a significant electronphonon interaction in them, although not so strong as might have been expected, based on the values of T_c (it is possible that the optical phonons also make a large contribution to λ).

3.3. Properties of the normal state

3.3.1. Optical conductivity. The unusual properties of HTSC materials often include an anomalous frequency dependence in the relaxation time in the normal state, measured by means of optical and photoemission techniques. Using the so-called generalized Drude formula, Schlesinger et al.¹⁰⁴ showed that the effective inverse of the relaxation time $\tau^*(\omega)$ which appears in this formula over a broad energy range from $\omega_1 = 30$ meV to $\omega_2 = 250$ meV depends linearly on the energy, $1/\tau^*(\omega) = \beta \omega$, with a coefficient $\beta \simeq 1$. At first glance, such a high upper boundary for the linear behavior of $1/\tau^*(\omega)$ contradicts the assumption that the damping of the electron states is due to phonons, since the value of ω_2 is considerably greater than the maximum phonon energy. Actually, as shown by Shulda *et al.*, 105 the assumption that the electron-phonon interaction is strong suffices to give good agreement between theory and the experimental data for T = 100 K (Ref. 104), while the reason for the anomalous behavior of $1/\tau^*(\omega)$ is related to the fact that this quantity is generally not proportional to the actual damping $1/\tau(\omega)$ of the single-particle states; this in turn saturates for values of ω larger than the maximum phonon frequency. Thus, in this case there is no need to bring in any additional (other than phonon) highfrequency excitations to explain the linear increase of $1/\tau^*(\omega).$

3.3.2. Electrical resistivity. As is well known, the behavior of the electrical resistivity of HTSC materials for $T > T_c$ has the following distinctive properties: high anisotropy, linear (or almost linear) temperature dependence of the resistivity $\rho_{ab}(T) = \rho_0 + \alpha T$ in the copper-oxide plane, unexpectedly very similar values of the slope $d\rho_{ab}(T)/dT$ for different metal-oxide compounds, and finally, a ratio \hbar/τ (where τ is the lifetime) which is proportional to k_BT with a proportionality coefficient of order unity.⁵² The fact that for the best samples ρ_0 it becomes negligibly small, while the linear behavior holds in a very broad temperature range, which in the opinion of Batlogg⁵² implies that scattering by phonons cannot be the principal source of resistivity. (Note also that there is no correlation between the value of α and the value of T_c .)

In this connection the most interesting observation involves the compound Bi2201 (Ref. 106), which exhibits linear behavior from 10 to 700 K (there are in addition some experimental data for the same metal oxide in Ref. 107).

The problem is that if we compare the data for HTSC materials and A15 compounds, then the values of the resistivity are of the same order of magnitude; but at sufficiently high temperatures the $\rho(T)$ curve for A15 compounds saturates, while the linear behavior for the metal oxides continues up to temperatures at which the compounds decompose.

In fact, however, the task of explaining the linear behavior of the electrical resistivity as a function of temperature in terms of the electron-phonon coupling is not so hopeless after all.^{3,108} It was analyzed in detail by Pickett,¹⁰⁸ who used a model for the electron-phonon interaction function of the metal oxides. Since these materials have a large number of low-frequency phonon excitations, the linear behavior which in ordinary metals begins for temperatures $T \ge \vartheta_D / 4$ (where ϑ_D is the Debye temperature) must be observed above $T \approx 30-40$ K (of course, there appears to be no possibility of explaining the linear behavior¹⁰⁶ from T = 10 K). On the other hand, the function $\alpha^2 F(\omega)$ is nonzero over a very broad range of energies (Figs. 5-7), and this may serve as a reason for the quasilinear behavior of the electrical resistivity up to very high temperatures.

But the problem is not just the functional form of $\rho_{ab}(T)$, it is also in the numerical values of the electronphonon coupling parameters. The procedure for finding the size of this coupling from the high-temperature behavior of $\rho(T)$ and the value of the plasma frequency $\omega_{\rm ph}$ was suggested by Gurvitch⁵³ and tested, in particular, in the A15 compounds. Nevertheless, even the earliest attempt to apply this technique to crystalline yttrium systems led to internal inconsistencies.⁵⁴ The values $\lambda = 0.2-0.4$ were found, which are clearly insufficient to obtain experimental values of T_c and the anomalously large ratios of $2\Delta/kT_c$ measured by tunneling and other techniques. Similar estimates by Batlogg also led to relatively low values of the constant λ . These results were re-examined in Ref. 109, using the newest experimental data for the electrical conductivity of single crystal Y-Ba-Cu-O samples and more carefully calculated Fermi velocities for this compound. The estimates¹⁰⁹ showed that the constant λ is mainly of order 1.5–1.7, while the electron mean free path at T = 300K is equal to 11 Å. Thus, some disagreements with the concepts of the electron-phonon interaction as the basic mechanism for superconductivity, at least in yttriumbarium metal oxides, can be completely excluded using the measurements of $\rho(T)$. Further confirmation of this viewpoint was obtained in Ref. 55, where YBa₂Cu₄O₈ single crystals were studied which had ideal structure in the ab plane. The plasma frequency was obtained from measurements in the optical region, and the behavior of $\rho(T)$ yielded the constant λ . In the *a* direction $\lambda_a = 3.64$ was found, and in the b direction $\lambda_b = 3.1$. Furthermore, it became clear that the temperature dependence of the electrical resistivity saturates for temperatures above 200 K. This means that the mean free path at these temperatures becomes comparable with the typical interatomic separation, which may be a consequence of the strong electronphonon interaction. The reason for the sharp contrast in the resistive properties of yttrium cuprates with 1-2-3 and 1-2-4 composition is still just as unclear as the behavior of $\rho(T)$ in superconducting metal oxides as a whole. We note also Ref. 89, in which the temperature dependence of the resistivity was calculated for Bi₂Sr₂CaCu₂O₈, using data on the spectral function $\alpha^2 F(\omega)$ obtained from photoemission experiments. These data demonstrated the existence of a high peak at 10 meV and a constant $\lambda = 8.67$. The calculated dependence of $\rho(T)$ was linear, beginning at 25 K, but the magnitude of the resistivity at $T = T_c$ was an order of magnitude greater than the experimental value.

3.3.3. Electron specific heat. As is well known, in the temperature range $k_{\rm B}T \ll E_{\rm F}$ (where $E_{\rm F}$ is the Fermi energy) the relation $C_e(T) = \gamma(T)T$ holds for the electron thermal conductivity of a normal metal. The electronphonon interaction determines the temperature dependence of γ ; when this interaction is very small, γ is constant and obeys the familiar linear law $C_e(T) = \gamma_0 T$. The latter relation holds for temperatures $k_{\rm B}T \ge \omega \simeq 0.25\bar{\omega}$ (here $\overline{\omega}$ is the typical phonon frequency), and has been estimated⁶ to hold even at $T \approx T_c$ for the superconducting metal oxides. But in the range of very low temperatures, where the electrons are heavily "dressed" with phonons, $\gamma(0) = \gamma_0(1+\lambda)$ holds. Thus, the electron-phonon coupling constant λ can be found from the relation⁶ $\lambda = (\gamma(0)/\gamma_0) - 1$. Kresin and Wolf⁶ suggested that the quantity γ_0 can be determined from the jump at $T = T_c$ in the specific heat $\Delta C = \beta \gamma T_c$, where $\beta \ge 1.43$ (see above, Sec. 3.1.4). Using the approximate expression for β in the strong-coupling theory and estimating $\gamma(0)$ from $\gamma(0) = (\partial \gamma / \partial H) H_{c2}$, Kresin and Wolf obtained $\gamma \approx 1.8-2.0$ for a lanthanum-strontium sample.⁶ This value of λ implies that the electrons interact fairly strongly with the lattice, although Kresin and Wolf felt that it was not enough for such large values of T_c . It would be interesting to apply the technique of Ref. 6 for calculating λ to other metal-oxide compounds.

3.3.4. Thermo-emf. An unusual property of the majority of metal oxide compounds with high T_c is the striking difference in the differential thermo-emf S_{ab} , for $T > T_c$ in the copper-oxygen plane between the measured value and that predicted by the free-electron model, $S = \text{const} \cdot T$. As shown by Kaiser and Mountjoy,³⁶ this behavior in such systems can be explained through the effect of the electron-phonon interaction. A similar effect had already been invoked previously to interpret the nonlinearities in the temperature dependence of the thermo-emf of ordinary metal alloys, but in this case the strength of the electron-phonon coupling estimated by means of this approach for some groups of electrons turns out to be much too large.³⁶

The reason for the effect of lattice vibrations on the S(T) dependence lies in the phonon renormalization of the basic electron properties determining the magnitude of the differential thermo-*emf*. At low temperatures the corresponding contribution associated with the electron-phonon interaction is substantial, but as T increases the



FIG. 16. The temperature dependence of the differential thermo-emf of the Bi₂Sr₂CaCu₂O_{8+ δ} system. The experimental data, measured mainly in the copper-oxygen plane, are shown by circles, squares, and crosses (for explanations see the work cited in Ref. 36). The solid trace corresponds to the calculated result,³⁶ and the broken trace to the bare (linear in T) contribution to the thermo-emf.

constant $\lambda(T)$ decreases and the dependence of S(T) generally approaches the usual (linear in T) result. If this contribution is small, then the phonon correction can make a significant change even at room temperatures (Fig. 16). As is clear from the above remarks, measurements of the thermo-emf offer a unique possibility for studying the temperature dependence of the electron-phonon coupling. Similar estimates³⁶ for the $S_{ab}(T)$ dependence in the copper-oxygen plane show that at least in yttrium, bismuth, and thalium systems for some carriers the EPI constant must be very large (at least 5). This implies³⁶ that there is strong anharmonicity associated with structural instabilities. It is interesting to note that the data obtained for directions outside the *ab* plane are much closer to the results for ordinary metals: in the majority of cases the derivative dS_c/dT remains positive up to room temperatures and the deviations from a linear behavior are slight. In terms of the model of Ref. 36 this means that in this situation the electron-phonon interaction is weaker than it is in the copper-oxygen plane. Although the behavior of the thermo-emf in this temperature range $T > T_c$ which was discussed above naturally does not prove that the superconductivity in HTSC compounds is of phonon origin, it is an additional indication that a strong electron-phonon interaction is present.

3.4. Microjunction spectra

To conclude the present section we return to the data from microjunction spectroscopy, obtained by studying the current-voltage characteristics of electrical microjunctions with direct conductivity. As in the tunneling spectra, the voltage dependence of the differential resistivity of microjunctions made from HTSC materials exhibits peaks in the region of phonon energies (these peaks are interpreted as a result of inelastic scattering of the carriers by vibrations of the crystal lattice).⁶⁴ Their position is well reproduced for a given microjunction, although the detailed shape differs somewhat from junction to junction. Still, some general



FIG. 17. Microjunction spectra of three La_{1.8}Sr_{0.2}CuO₄/Cu junctions. Here $F(\omega)$ is the density of phonon states found from neutron data.⁶⁵

properties of this structure have been discovered for various samples. Thus, for lanthanum-strontium cuprates⁶⁵ it has been found that at energies above 90-100 meV (i.e., outside the phonon spectrum) the strength of the maxima in (dV/dI)(V) drops sharply, and the location of the more pronounced maxima in the range from 20 to 50 meV agrees with that of the maxima in the phonon density of states determined from neutron measurements (Fig. 17). The amplitude of the spikes observed in (dV/dI)(V) at low temperatures is up to 10% of the background value, which is at least an order of magnitude greater than the amplitude of the analogous maxima for Ta/Cu junctions.⁶⁵ If we assume that the observed spikes are the result of carrier scattering by phonons, then this means that the electron-phonon interaction is extremely large, at least in La-Sr-Cu-O, and according to Ref. 64 can be responsible for the large values of $T_{\rm c}$.

4. CONCLUSION

Comparison of the tunneling data for various metaloxide compounds, including those with no copper ions, shows that lattice vibrations play a role in the measured properties. But why do the lattice vibrations of the superconducting metal oxide still manifest themselves in its tunneling spectra, despite the vanishingly small depth of penetration $l_{\rm ph}$?

One possible approach to this problem is to take into account the effect of the proximity of the normal layer adjacent to the barrier on the surface of the cuprate and the bulk superconductor (see Fig. 4 in Ref. 76, and Ref. 84). It has recently been discovered that the depth of penetration of the superconductivity is relatively large in semiconducting metal oxides placed in immediate contact with HTSC material (see the material cited in Ref. 77). Perhaps this quantity is large in the present case as well, and thus superconductivity exists right at the interface between the insulator and the conducting layer. On the other hand, the depth to which the nearby layer is felt usually exceeds the corresponding value of $l_{\rm ph}$ for a pure superconductor (see Sec. 5.6 in Ref. 5). This produces additional advantages (and strange as it may seem, difficulties) for tunneling studies of HTSC materials by applying additional layers to the surface.

It should be emphasized that the fact that phonon peaks appear in the tunneling conductivity in no way proves that the electron-phonon mechanism is the dominant one in these superconductors. The only way to prove that would be to reproduce the electron-phonon interaction function numerically. However, almost all published attempts to reconstruct the function $\alpha^2 F(\omega)$ for HTSCs have failed to stand up to criticism. As long as the publications do not provide a detailed analysis of the experimental data underlying the calculations of $\alpha^2 F(\omega)$ or any proof that all the rigid requirements on the object of these studies are satisfied there is no reason to have confidence in the quantitative side of such treatment, and, even more so, in the far-reaching conclusions about the nature of the superconducting mechanisms.

The tunneling effect is a highly informative experimental technique, and an actual tunneling experiment fortunately does not reduce to just taking the current-voltage characteristic and its derivatives. In practice it is necessary to be able to include the contributions of various current transport mechanisms in metal-metal oxide junctions and substantiate the dominant role of the tunneling effect. This cannot always be done everywhere. By the way, the concept of a "good" or "bad" tunneling junction, generally speaking, is meaningless and reflects rather a certain intellectual level of the investigator. It is precisely for this reason that reconstruction of the EPI function is one of the highest arts of the experimentalist.

Let us comment about one characteristic feature of the tunneling data for high-temperature superconductors: the anomalous (nonanalytic at zero voltage) dependence of the differential conductivity as a function of voltage, $\sigma(V) = \sigma_0 + \alpha |V|$ (see Refs. 74, 80, 81 and the work cited therein). The discovery in Ref. 74 of a correlation between the magnitude of α and the value of the critical temperature $T_{\rm c}$ for four copper-free metal oxides with $T_{\rm c}$ varying from < 1 K for BaPbO₃ to 30 K for Ba_{1-x}K_xBiO₃ is important. According to Dynes et al.,74 the linear dependence is the result of the strong renormalization of the spectral properties of the charge carriers resulting from multiparticle effects. In our opinion, the unique relation between α and T_c implies that the quantity α is a measure of the strength of the coupling for the mechanism which is responsible for superconductivity in these materials.

One possible way to reveal this mechanism is to compare the calculated and the experimental data. However, even here things are not clear. According to some treatments,^{82,86,87} assumptions about the existence of an intermediate electron-phonon coupling in the cuprates suffices to explain high-temperature superconductivity in them; according to other calculations (e.g., Andersen *et al.*⁸³) the interaction with the lattice vibrations is really quite large $(\lambda \approx 1)$, but this cannot be the only reason for large values of T_c in these compounds. As for nonphonon mechanisms for superconductivity, we note in this connection the possible role of antiferromagnetic spin fluctuations,⁷⁸ which lead in particular to marked anisotropy of the superconducting properties. It is of interest to note that the best tunneling results (in terms of observing superconducting behavior) have been obtained for those metal oxides in which either the copper ions are absent $(Ba_{1-x}K_xBiO_3)$ or the magnetic interactions are weakened $(Nd_{2-x}Ce_xCuO_{4-y})$.⁷⁹

And of course, the electron-phonon interaction cannot be a universal key to all riddles posed by metal-oxide superconductors. In particular, as was correctly noted by Ginzburg and Maksimov,³ phonon concepts are inadequate to describe the temperature dependence of the Hall effect and the magnetic susceptibility, and they are completely unsuited for reproducing the phase diagrams of these compounds. This is true, in particular, of the transition to an antiferromagnetic insulating state.

^{*}2.5. Omitted from Russian text.

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