

caused by the hyperfine splitting of the transition due to the interaction with a spin of the ^{17}O nucleus were observed. The width of the holes (≈ 50 kHz) was close to the inverse time of flight of the molecules through the region of the electromagnetic field in the resonator, which determines the limiting spectral resolution of the spectrometer.

The high sensitivity of the spectrometer made it possible to measure a number of transitions in the rotational spectra of the R-CO complexes in the 100–140 GHz range, where R = Ne, He, N₂, and H₂. So far, only spectra of Ne-CO have been observed in the microwave region (in the centimeter wavelength region). Figure 3 shows the recording of the $Jl = 110-000$ transition (J is the total rotational moment, j is the rotational moment of CO, and l is the rotational moment for CO retarded) in the H₂-CO complex. The transition frequencies were determined with an accuracy of 50–100 kHz, which is sufficient for the search for spectral lines of these complexes in space. Preliminary experimental results were published in [4].

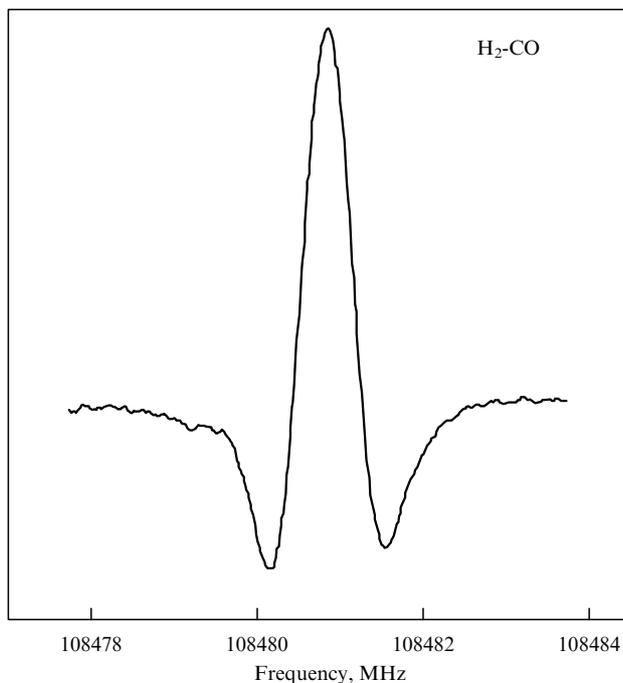


Figure 3. Second derivative of the absorption signal at the rotational transition of the H₂-CO complex.

Note that spectroscopy of these complexes is of great interest for the study of Van der Waals forces, because it permits the measurement of the inertia moment and, hence, the distance between monomers with high accuracy. At present, these experiments are being continued.

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Infrared spectroscopy of new spin-Peierls compounds

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The paper presents a review of studies of the quasi-one-dimensional crystals CuGeO₃ and NaV₂O₅ with the spin-Peierls transition, performed during two last years in the Department of Solid-State Spectroscopy of the Institute of Spectroscopy, RAS.

First, we briefly explain the meaning of the spin-Peierls transition and consider its features of interest. The spin-Peierls transition represents a phase transition in a system of Heisenberg antiferromagnetic chains of half-integer spins interacting with a three-dimensional phonon field [1]. After the phase transition, magnetic atoms in the chain come close together in pairs and form nonmagnetic dimers. In this case, the magnetic susceptibility tends to zero isotropically over all directions. A gap appears in the spectrum of magnetic excitations, which separates the ground singlet state from the first excited triplet state. The gain in the magnetic energy $\Delta E_{\text{mag}} \sim -u_0^2 |\ln u_0|$ (here, u_0 is the amplitude of atomic displacements along the chain) can exceed the loss of the elastic energy $\Delta E_{\text{latt}} \sim u_0^2$ caused by the lattice deformation. Such a transition represents a magnetic analog of the Peierls transition induced by the electron – phonon interaction in quasi-one-dimensional conducting crystals.

The concept of the spin-Peierls transition was suggested as early as 1962, and later the theory was developed. However, attempts to detect this transition were not successful for a long time, although a great number of quasi-one-dimensional magnetics are known. The reason was a competing interchain magnetic interaction resulting in three-dimensional antiferromagnetic order. The spin-Peierls transition was experimentally detected only in 1975 in a complex organic compound TTF-CuS₄C₄(CF₃)₄ containing chains of Cu²⁺ ions ($S = 1/2$). Attempts to obtain this compound in the form of sufficiently large single crystals have failed, and its study involves difficulties. The same is true for several other organic spin-Peierls compounds discovered later. For this reason, the first observation of the spin-Peierls transition in a comparatively simple inorganic compound CuGeO₃ reported in 1993 [2] aroused great interest. Note that the study of low-dimensional magnetism in oxides of transition metals became especially urgent in those years in connection with the problem of high-temperature superconductivity. The matter is that, first, an important element of the structure of new high-temperature superconductors is copper-oxygen planes and chains and, second, magnetism and superconductivity are strongly related in them.

In 1996, a second inorganic compound, NaV₂O₅, with the spin-Peierls transition was found [3]. Both CuGeO₃ and NaV₂O₅ can be obtained in the form of large stable single crystals of good quality and can be studied by different methods. The Table presents the transition temperature T_c ,

Table. Energy parameters of CuGeO₃ and NaV₂O₅.

Crystal	T_c , K	J , K	Δ , meV
CuGeO ₃	14	140	2.1
NaV ₂ O ₅	35	560	9.8

the values of the exchange integral J in the Hamiltonian of the intrachain interaction $\mathcal{H} = \sum_i JS_i S_{i+1}$ obtained from magnetic measurements, and the values of the gap Δ in the spectrum of magnetic excitations found from neutron experiments. X-ray scattering studies revealed at $T < T_c$ superstructure reflections, which correspond to the doubling of the crystallographic cell along the direction of magnetic chains.

What can be found from optical studies? First, information can be obtained on normal vibrational modes of a crystal lattice with zero wave vector ($\mathbf{k} = 0$), in particular, on the vibrational modes that appear at $T > T_c$ due to ‘folding’ of the Brillouin zone upon the structural phase transition accompanied by the cell doubling. Second, one can study the spectrum of magnetic excitations and its change upon the spin-Peierls transition, by observing two-magnon processes at which a photon creates two magnons with wave vectors \mathbf{k} and $-\mathbf{k}$. Third, one can study the spectrum of electronic excitations.

We studied single crystals of CuGeO_3 grown and characterized in M V Lomonosov Moscow State University (MSU) and of NaV_2O_5 grown in Tokyo University and characterized in MSU and P L Kapitsa Institute for Physical Problems, RAS. The polarized transmission spectra of thin samples at temperatures from 5 to 300 K and reflection spectra at room temperature were detected with a BOMEM DA3.002 Fourier spectrometer with a resolution up to 0.05 cm^{-1} in the spectral range from 25 to 25 000 cm^{-1} .

We found two weak absorption lines in the far-IR spectrum of CuGeO_3 , which exist below the transition temperature $T_c = 14 \text{ K}$, and showed that they are related to ‘folded’ vibrational modes [4]. A broad band located in the red spectral region, which corresponds to the electronic $d-d$ transitions in the Cu^{2+} ion [5], does not change upon the phase transition within the accuracy of our measurements. Its intensity continuously decreases with decreasing temperature because the $d-d$ transition is forbidden in a static crystalline field (the local symmetry of the $\text{Cu}^{2+} - C_{2h}$ position includes the inversion center) and becomes allowed due to vibrations [5]. According to the symmetry, two-magnon absorption in CuGeO_3 is forbidden.

The second compound, NaV_2O_5 , proved to be very interesting. As was reported in a pioneering paper [3], its quasi-one-dimensional magnetic properties are caused by chains of V^{4+} ions ($S = 1/2$) directed along the b -axis, which are separated by chains of nonmagnetic V^{5+} ions. The absorption spectrum of NaV_2O_5 in the far-IR region substantially changes at the phase transition temperature.

First, many new lines appear [6]. The temperature dependence of the intensity of most these lines is the same as that of the intensity of superstructure reflections in X-ray scattering, i.e., it reflects the temperature dependence of the order parameter. All the lines shift and broaden near the transition temperature. For comparison, the frequencies and widths of new lines of CuGeO_3 are invariable.

Second, below the transition temperature the crystal bleaches in one of the polarizations ($\mathbf{E}||\mathbf{a}$), at least, in the spectral region between 25 and 300 cm^{-1} . Third, the shape of the narrow absorption line located at 90 cm^{-1} against the bleaching background changes from the dispersion contour, which is typical for the Fano resonance between a discrete state and a continuum, to a normal symmetrical Lorentzian contour [6] (see Figure).

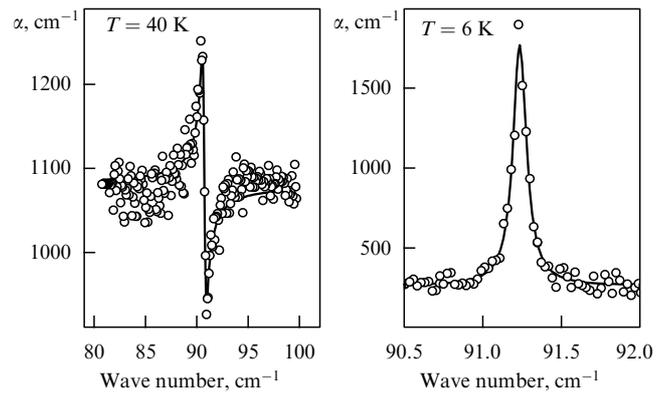


Figure. Part of the polarized ($\mathbf{E}||\mathbf{a}$) absorption spectrum of a NaV_2O_5 single crystal in the far-IR region at temperatures above and below T_c . The circles are experimental data, and the solid curve is the approximation by a Fano contour $\alpha = H(q^2 + 2q\xi - 1)/(1 + \xi^2)$, $\xi = (\omega - \omega_0)/\gamma$ with parameters $\omega_0 = 90.7 \text{ cm}^{-1}$, $\gamma = 0.2 \text{ cm}^{-1}$, $q = -1.0$ (for $T = 40 \text{ K}$) and by a Lorentzian contour with the half-width $\gamma = 0.1 \text{ cm}^{-1}$ (for $T = 6 \text{ K}$).

We assigned the broad absorption band in the far-IR region to two-magnon transitions. The bleaching in the region of its long-wavelength wing can be naturally explained by the opening of the gap in the spectrum of magnetic excitations upon the spin-Peierls transition. The narrow absorption line is related to a vibrational mode of a crystal lattice, which interacts with a continuum of magnetic excitations at $T > T_c$ [6]. The line shape (characterized by the parameter q , see Figure) yields information on the magnitude of this interaction.

However, in order to extract the constant of spin-phonon interaction (which induces the spin-Peierls transition) from our experimental data, the corresponding theoretical model is required. Its development was interrupted by the report of German crystallographers [7] which suggested that the structure of NaV_2O_5 is most likely described by the centrosymmetric D_{2h}^{13} group.

Although the structure topology is the same for both groups, the new centrosymmetric group excludes the existence of alternating $\text{V}^{4+} - \text{V}^{5+}$ chains, and hence, the one-dimensional magnetic properties of NaV_2O_5 cannot be related to them. Because the choice between the two above groups is very important for the interpretation of magnetic, electronic, and optical properties of NaV_2O_5 and the phase transition in this compound, we performed an independent verification. Studies of IR and Raman spectra give information on the presence or absence of the inversion center, because the selection rules for these spectra are substantially different. Our careful measurements of IR and Raman spectra for all possible polarizations and also the results of calculations of the lattice dynamics of NaV_2O_5 showed that the centrosymmetric D_{2h}^{13} group is more probable [8].

This means that the following interpretation of the quasi-one-dimensional properties of NaV_2O_5 suggested in Refs [7, 9] should be probably adopted: the d electron is ‘smeared’ over the molecular orbital of a linear $\text{V}-\text{O}-\text{V}$ ‘molecule’ elongated along the a -axis. The intermolecular interaction results in the formation of ‘ladders’ along the b -axis, which weakly interact with each other. The phase transition at 35 K was treated in Ref. [9] as the usual spin-Peierls transition in a system of chains of spins $S = 1/2$, ‘seated on rungs of the ladder’ rather than localized.

However, a recent NMR study of ^{51}V showed that vanadium has two positions, V^{4+} and V^{5+} , below 35 K [10], i.e., charge ordering takes place. The theoretical consideration of the Coulomb repulsion between the electrons results in a linear (along the b -axis) ordering in the V^{4+} and V^{5+} chains, similar to a scheme suggested in Ref. [11]. However, the interaction with lattice deformations can make zigzag charge ordering more advantageous [12]. The simultaneous consideration of the Coulomb, electron – phonon, and spin – phonon interactions results in a great variety of types of charge ordering, depending on the relative magnitudes of these interactions [13]. What variant is realized upon the phase transition in NaV_2O_5 crystals remains to be answered in further experiments. The results of our recent study of the dielectric anomaly observed in the microwave and IR regions upon the phase transition in NaV_2O_5 suggest the presence of antiferroelectric ordering [14].

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New developments of optical spectral instruments in the Institute of Spectroscopy, RAS

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In a report presented in 1993, new supersensitive methods and optical spectral instruments developed in the Institute of Spectroscopy, RAS, and their applications in high technologies and ecology were discussed. Now, we consider new results obtained by means of these methods.

We consider briefly the results obtained by the method of laser atomic fluorescence spectrometry suggested and

developed by M A Bol'shov, V G Koloshnikov, A V Zybin, and S N Rudnev and LAFAS spectrometers with electrothermal atomization of a substance based on this principle. The direct analysis of ice samples in the Antarctic and the Northern Hemisphere aimed to study global changes in the climate and the consequences of practical activities of human beings gave new impressive detection limits for Cd, Bi, and Pb at a level of 3.6–0.2 fg (0.18–0.01 ppt). In collaboration with French researchers, the concentration of Cd was measured in the Antarctic ices depending on their age and its correlation with changes in the Earth's climate over the last 155 thousands years was monitored. Similar measurements were also performed for snow and ice in the Northern Hemisphere. It was found that at least 95% of the cadmium in layers up to 30 years old were of an anthropogenic nature.

Another supersensitive method for detecting elements is multistep resonance photoionization of atoms suggested by V S Letokhov and then developed by V I Mishin, G I Bekov, and Yu A Kudryavtsev. This method was recently used most successfully for studies in the field of laser-nuclear spectroscopy. The impressive feature of this method, provided the ionization is performed in a hot cavity or capillary, is the extremely high chemical selectivity, which is sufficient for suppression of the isobaric background, and the high ionization efficiency, which was successfully demonstrated many times on the ISOLDE accelerator with a mass separator (CERN).

An ion source producing ions selected over Z is based on laser ionization of atoms with short-lived nuclei in a capillary, which are formed in targets upon their bombardment by proton beams. This source consists of 1–2 copper vapor lasers with a total output power of up to 55 W, 2–3 dye lasers (above 1 W), and a nonlinear frequency converter (above 100 mW). The radiation from lasers tuned to the resonance transitions of isotopes under study passes through the window of a magnet of a mass separator and is focused at a distance of about 20 m onto the input aperture of a capillary. The capillary is usually a cylinder made of a high-melting metal with channels in its walls for the diffusion of products of nuclear reactions produced on the target.

The method of a laser ion source has recently been applied for producing chemically selective Mn ion beams for Mössbauer experiments, obtaining a neutron deficient Sn-101 isotope and long-lived Ni isotopes, for studying their energy spectra, producing beams of Ag, Be, Zn, Cd, and Cu, as well as, in problems of the materials technology, astrophysics, and nuclear physics. A recent achievement was the discovery and study by V I Mishin and V N Fedoseev in collaboration with ISOLDE of a strongly neutron excess silver isotope Ag-129, which is one of the key isotopes involved in the r -process proceeding inside stars and is responsible for the synthesis of heavy elements in the Universe.

In 1998, the Institute finished the development of a completely automated laser ion source intended for the same aims of laser-nuclear spectroscopy. All the components of this sophisticated laser complex — dye lasers with fast precision wavelength tuning, a portable precision wavemeter, a precision two-coordinate beam director, a spectrum analyzer, and a system of ion current detection, were improved over many years and represent completed instruments produced (it is important) by the Pilot Production Division of the Institute of Spectroscopy, RAS.