Optical absorption in the spin-Peierls cuprate $CuGeO_3$

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This paper discusses the optical absorption in polarized light of single crystals of $CuGeO_3$ in the 2000–30 000-cm^{-1} (0.25–3.7-eV) region. The absorption edge in the UV part of the spectrum (3.1 eV for **E**||**c** and 3.4 eV for **E**||**b**) is determined, and an absorption band with a width of 0.5 eV is found at the boundary between the red and IR regions. The features on the absorption curve in the red region are compared with the results of a band-structure calculation carried out earlier by other authors. © *1996 American Institute of Physics.* [S1063-7761(96)02312-8]

The quasi-one-dimensional germanium cuprate $CuGeO_3$ (space group *Pbmm*) attracted the attention of researchers after a spin-Peierls transition (at a temperature of $T_{sp}=14$ K) was detected in it, the first found in an inorganic compound.[1] Such a transition in a system of homogeneous Heisenberg antiferromagnetic chains with half-integral spin, in which the atoms in each chain approach each other in pairs and form a singlet ground state removed from the first excited (triplet) state by an energy gap, had been observed until then only in organic compounds. From magnetic measurements,[1] the gap in $CuGeO_3$ at zero temperature was estimated as $E_g=2.07$ meV. Neutron studies[2] gave a similar value of $E_g=2.0\pm0.1$ meV. Optical EPR with far-IR lasers was used by Ref. 3 to find two gaps, $E_{g1}=1.9\pm0.4$ meV and $E_{g2}=4.7\pm0.9$ meV, which presumably occur at different points of the Brillouin zone. Band-structure calculations for $CuGeO_3$ by two different methods[4,5] showed that dimerization of the copper atoms in the chains (oriented along the crystal's **c** axis) causes a gap to open at the Fermi level, provided that the atoms in adjacent chains shift in opposite phases. This is precisely the type of shift that was supported by the neutron studies of Ref. 6. Reference 4 proposed a complete band-structure diagram for $CuGeO_3$ in a wide energy range at temperatures above and below T_{sp}. It is of interest to study the optical absorption of $CuGeO_3$ in order to compare it with the band calculations of Refs. 4 and 5 and to search for possible changes during the spin-Peierls transition.

This paper discusses the optical absorption in polarized light of single crystals of $CuGeO_3$ in the frequency region 2000–30 000 cm^{-1} (0.25–3.7 eV). Transparent blue single crystals were grown by slow cooling from a nonstoichiometric composition with an excess copper oxide concentration. Samples were prepared from these crystals, with dimensions of 4×4 mm along the *b* and *c* axes and from 13 μm to 1.2 mm along the *a* axis.

Figure 1 shows the absorption spectrum of $CuGeO_3$ at room temperature. An absorption band about 0.5 eV wide can be seen at the boundary of the red and IR region. This is followed by the transmission window corresponding to the blue color of the $CuGeO_3$ crystals and then by the fundamental absorption edge in the UV region. There is no absorption band below the red band in the entire frequency region under investigation. Note the appreciable dichroism of the absorption in the *bc* plane. It is about 20% at the maximum of the red band. The UV absorption edge is about 0.3 eV higher for **E**||**b** than for **E**||**c** polarization. The refractive index is also polarization-dependent: $n_c/n_b=\Delta_b/\Delta_c=1.08\pm0.01$ ($\Delta_b=dn_b/2$ is the period of the interference pattern observed in transmitted light for **E**||**b**, Δ_c is the same for **E**||**c**, and *d* is the sample thickness). In the wavelength region near 1 μm (1.25 eV), we find $n_c=2.35\pm0.10$. This value was found by two methods: by measuring Δ_c and d and from the transmission of a thin sample outside the absorption band, where the following relationships are satisfied:

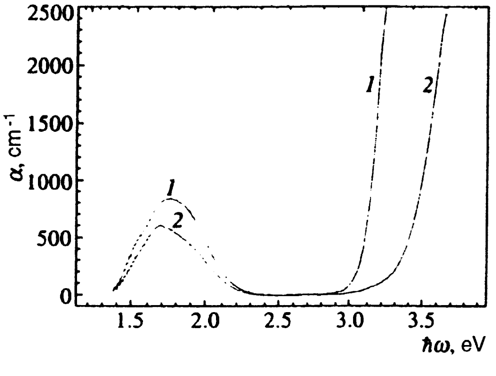

FIG. 1. Absorption spectrum of a single crystal of $CuGeO_3$ at room temperature in two polarizations (Specord M400 spectrometer); *1*—**E**||**c**, *2*—**E**||**b**.

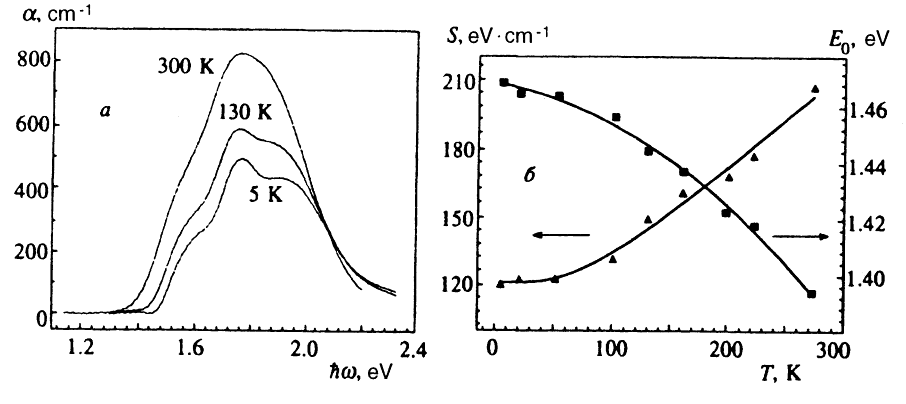

FIG. 2. (a) Red absorption band of $CuGeO_3$ for E||c at various temperatures (BOMEM DA3.002 Fourier spectrometer) and (b) temperature dependences of its long-wavelength edge E_0 (squares) and area S (triangles). The solid curve for the area is calculated from $S(T)=121+95[\exp(148/kT)-1]^{-1}$.

$$t=\frac{1-R}{1+R},\quad R=\frac{(n-1)^2}{(n+1)^2}.$$

The anisotropy of the absorption and refraction of light in the *bc* plane is evidently associated with crystal anisotropy.

It is shown in Fig. 2 how the red absorption band varies for E||c as the crystal is cooled. The long-wavelength edge shifts toward higher energies in the temperature interval 273–100 K with a mean rate of 3.6×10^{-4} eV/deg typical of semiconductors, the total absorption appreciably decreases, and structure appears in the spectrum.

Let us compare the observed features of the $CuGeO_3$ absorption spectrum with the band diagram proposed in theoretical papers.[4,5] Figure 3 reproduces a figure from Mattheiss's article[4] with the results of his energy-band calculations. Note the almost degenerate pair of narrow bands (about 1 eV) close to the Fermi level. These one-dimensional half-filled conduction bands, like the series of close-lying, narrow upper valence bands, are formed by the two CuO_2 chains in the unit cell.[4,5]

It is natural to ascribe the red absorption band to transitions between states of the group of upper occupied valence bands and unoccupied states of the lower conduction band. These transitions are genetically associated with forbidden intraconfiguration d–d transitions in Cu^{2+} ions, which is why they have relatively low intensity. The increase in absorption intensity at increased temperature corresponds to the removal of the forbiddenness because of interaction with odd modes. Approximating the temperature dependence of the band intensity by the factor $[\exp(\hbar\omega/kT)-1]^{-1}$ (see Fig. 2b), we get $\hbar\omega=18.4$ meV, which can be regarded as the mean energy of the photons that participate in the optical transition.

Keeping in mind that the accuracy of the calculations is

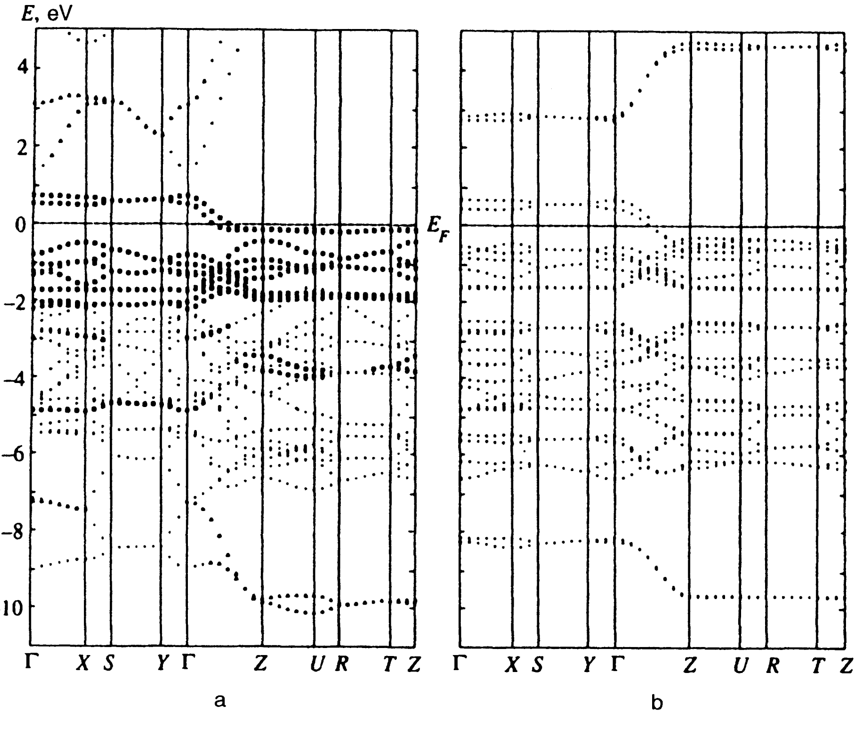

FIG. 3. Energy bands of $CuGeO_3$ calculated[4] by the method of associated plane waves (a) and by the strong-binding method (b).

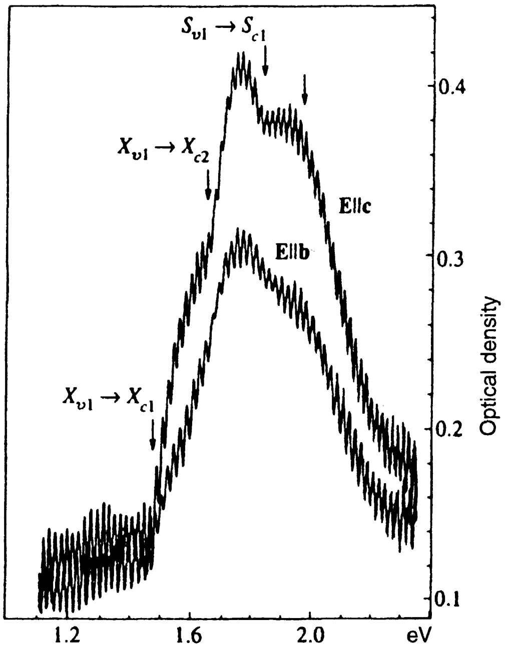

FIG. 4. Comparison of the features in the low-temperature absorption spectrum of $CuGeO_3$ with transitions at the singular points of the Brillouin zone. $T=3$ K, $d=13$ μm. Interference is seen in the sample.

no better than 0.5 eV, we should nevertheless point out that, in calculations by the strong-coupling method,[4] the group of upper valence bands, with an overall width of about 1.3 eV, is removed from the lower-lying bands by a gap of about 1 eV, so that a gap of between 2.3 and 3.2 eV should be observed in the optical spectrum (see Fig. 3), which agrees with experiment.

We now consider the features on the low-temperature contour of the red band, which can be associated with singularities of the combined density of states close to the singular points of the Brillouin zone (Fig. 4). Table I shows the calculated energies of the transitions at the singular points of the Brillouin zone.[4,5] The bands are numbered in order from the Fermi level, going up (the conduction bands) and down (the valence bands). The direct absorption edge, according to the calculations of Refs. 4 and 5, corresponds to transitions at point X, and the indirect absorption, with a similar value of the gap, corresponds to $Z \rightarrow \Gamma$ or $X \rightarrow \Gamma$ transitions. Unfortunately, the authors of Refs. 4 and 5 did not indicate the irreducible representations under which the wave functions transform, and therefore the selection rules for the optical transitions are not known.

TABLE I. Calculated[4,5] and experimental energies of the optical transitions at the singular points of the Brillouin zone of $CuGeO_3$.

	E, eV		
Optical transition	Ref. 4	Ref. 5	Experiment
$X_{v1} \rightarrow X_{c1}$	0.95	1.32	1.48
$Z_{v1} \rightarrow \Gamma_{c1}$	0.99	1.48	-
$X_{v1} \rightarrow \Gamma_{c1}$	1.02	1.30	-
$X_{v1} \rightarrow X_{c2}$	1.17	1.65	1.67
$Z_{v1} \rightarrow \Gamma_{c2}$	1.20	1.80	-
$X_{v1} \rightarrow \Gamma_{c2}$	1.22	1.63	-
$S_{v1} \rightarrow S_{c1}$	1.27	1.73	1.83
$\Gamma_{v1} \rightarrow \Gamma_{c1}$	1.33	1.80	-
$X_{v2} \rightarrow X_{c1}$	1.48	1.87	-
$\Gamma_{v1} \rightarrow \Gamma_{c2}$	1.53	2.12	-
$\Gamma_{v2} \rightarrow \Gamma_{c1}$	1.59	2.17	1.98
$Y_{v1} \rightarrow Y_{c1}$	1.61	2.25	-
$X_{v2} \rightarrow X_{c2}$	1.68	2.17	-
$Z_{v1} \rightarrow \Gamma_{c3}$	1.88	3.36	-
$X_{v1} \rightarrow \Gamma_{c3}$	1.90	3.20	-
$\Gamma_{v1} \rightarrow \Gamma_{c3}$	2.12	3.76	3.1
$\Gamma_{v2} \rightarrow \Gamma_{c3}$	2.40	4.17	3.4

A sharp absorption threshold at $E_{g1}=1.48$ eV is seen in the spectrum with polarization **E**||**c**, with the absorption close to the threshold being closely approximated by the dependence $\alpha E \propto \sqrt{E-E_{g1}}$, characteristic of allowed transitions. One more sharp step is observed in the absorption spectrum at $E_{g2}=1.67$ eV. We compare the E_{g1} and E_{g2} thresholds in the spectrum for **E**||**c** with direct transitions at point X of the Brillouin zone between the upper valence band and the almost degenerate pair of lower flat conduction bands. The experimental value of $E_{g2}-E_{g1}=0.19$ eV agrees well with the calculated splitting of this pair of bands, $\Delta E=0.2$ eV (Ref. 4) or 0.3 eV (Ref. 5). The absorption edge in the **E**||**b** polarization is not sharp, the absorption is smaller in magnitude, and it depends quadratically on the photon energy in the 1.5–1.7-eV region. The contribution from indirect transitions is apparently substantial here.

The spectral dependence of the absorption coefficient for **E**||**c** contains distinctly visible features at 1.83 eV, of the maximum type, and at 1.98 eV, of the saddle-point type. For **E**||**b**, these features are shifted and blurred. Since, above the threshold, contributions to the absorption come from numerous interband transitions that are close in energy (see Table I), it is hard to correlate the observed features with definite transitions. We tentatively ascribed the first of these features to the next transition in calculated energy: $S_{v1} \rightarrow S_{c1}$.

The two observed absorption edges in the UV region, separated by an interval of about 0.3 eV, are apparently associated with the $\Gamma_{v1} \rightarrow \Gamma_{c3}$ and $\Gamma_{v2} \rightarrow \Gamma_{c3}$ transitions, allowed in different polarizations, from the two upper valence bands at point Γ, separated from each other by 0.28 (Ref. 4) or 0.40 eV (Ref. 5), to the first unfilled conduction band. The absorption tail may be associated with the indirect transitions $Z_{v1} \rightarrow \Gamma_{c3}$ and $X_{v1} \rightarrow \Gamma_{c3}$.

We detected no difference in the absorption in the frequency region 0.25–2.2 eV at $T=20$ K $>T_{sp}$ and $T=5$ K $<T_{sp}$. The optical transitions between the new electron bands that appear after the spin-Peierls transition apparently fall into the region of the red band and change its shape so insignificantly that our measurements are not accurate enough to show it.

The identification that we carried out should be regarded as preliminary. We hope that our work will stimulate further theoretical consideration of the band structure of $CuGeO_3$.

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