Submillimeter vibrational spectra of the superionic conductor $RbAg_4I_5$

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The IR vibrational spectrum of the superionic conductor $RbAg_4I_5$ at frequencies $\sim 16\ cm^{-1}$ has been observed to split up into a series of narrow lines at low temperatures. The splitting is apparently caused by a localization of sulfur ions at nonequivalent positions in the γ phase.

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Dielectric measurements have been carried out for the superionic conductor $RbAb_4I_5$ over the frequency range 6-20 cm^{-1} and from room temperature down to 4.2 K. The purpose of the experiments was to obtain data on the temperature dependence of the specific lattice excitation in $RbAb_4I_5$ which has been observed repeatedly at 15

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cm^{-1} in the IR and Raman spectra[1,2] and in neutron scattering spectra.[3] The phonon spectra of superionic conductors at these frequencies are known to interlock with vibrational spectra of free current carriers. The observed mode is very probably a direct manifestation of an interaction of mobile silver ions with a rigid crystal framework.

The most interesting properties of $RbAs_4I_5$ are its high ionic conductivity at room temperature ($\sigma \approx 0.27$ mho/cm; Ref. 4) and the occurrence of two structural phase transitions[5] at $T_1 = 208$ K and $T_2 = 122$ K, which take the crystal from the α phase and put it in the β phase (T_1) and then take it from the β phase and put it in the γ phase (T_2). The phase transition at T_1 has little effect on the electrical properties of $RbAg_4I_5$, while the static conductivity falls off by two orders of magnitude at T_2, where the crystal goes into the γ phase.[5]

We used an Epsilon-2 submillimeter spectrometer and the method of Ref. 6 to measure the frequency dependence of the energy transmission coefficients $T(\nu)$ of a parallel-plate $RbAg_4I_5$ sample at various temperatures. We also measured the corresponding phase shift of the wave in the sample, $\psi(\nu)$. Using $T(\nu)$ and $\psi(\nu)$, and solving the system of nonlinear equations for the optical constants, we calculated the dielectric spectra $\epsilon'(\nu)$ and $\epsilon''(\nu)$ and the dynamic conductivity $\sigma(\nu) = \nu \cdot \epsilon''(\nu)$. The $RbAg_4I_5$ samples were grown from a single crystal with well-defined natural faceting along the [110] plane with dimensions of $10 \times 10 \times 0.3$ mm. No anisotropy of the dielectric properties of $RbAb_4I_5$ was detected[1)] in this plane in any of the three phases: α, β, or γ.

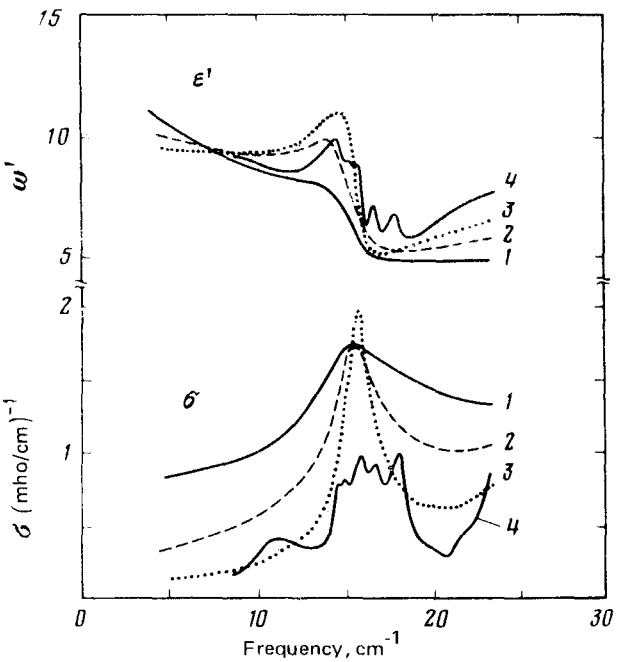

FIG. 1. Submillimeter spectra of the dielectric function, $\epsilon'(\nu)$, and the conductivity, $\sigma(\nu)$, of $RbAg_4I_5$. 1–4–298, 184, 123, and 112 K, respectively.

Figure 1 shows the overall temperature dependence of the submillimeter vibrational spectra of $RbAg_4I_5$. At room temperature the most prominent feature is a damped resonant absorption line at $\sim 16\ cm^{-1}$, evidently the same line which has been observed previously in IR spectra but which was almost an order of magnitude broader in the previous measurements.[1] The quality factor of this line increases significantly with decreasing temperature in the α and β phases, and its intensity increases (curves 1, 2, and 3).

Another common feature of the spectra of the α and β phases is a broad absorption wing, which is present over the entire frequency range but particularly noticeable at $\nu \lesssim 10\ cm^{-1}$, where the resonant absorption mechanism is essentially unseen in the spectra. The level of this diffuse background also depends strongly on the temperature, falling off with decreasing temperature.

The transition from the α phase to the β phase has almost no effect on the submillimeter spectra; it changes σ by less than 1% at $T = 208$ K.

At the transition to the γ phase there is a radical change in the spectrum. The diffuse absorption disappears entirely (curve 4 in Fig. 1), and the nature of the resonant absorption changes abruptly: The mode at 16 cm^{-1} splits into several components. Figures 2 and 3 show the subsequent behavior of these components as the crystal is cooled, in the γ phase. Finally, at $T = 4.2$ K, we see intense, well-resolved lines in the spectra. Their widths are less than 0.1 cm^{-1} in some cases and generally extremely small in comparison with the widths of the ordinary lattice modes.

In a first approximation, these experimental results can be interpreted as follows. The diffuse absorption in the α and β phases is evidently an absorption by free carriers: silver ions, Ag^+. The resonant peak at 16 cm^{-1} is also due to a motion of Ag^+ ions, but in this case vibrations in shallow local potential minima. The decrease in the conductivity with decreasing temperature in the α and β phases at low frequencies results from a lowering of the average energy of the thermal fluctuations, which re-

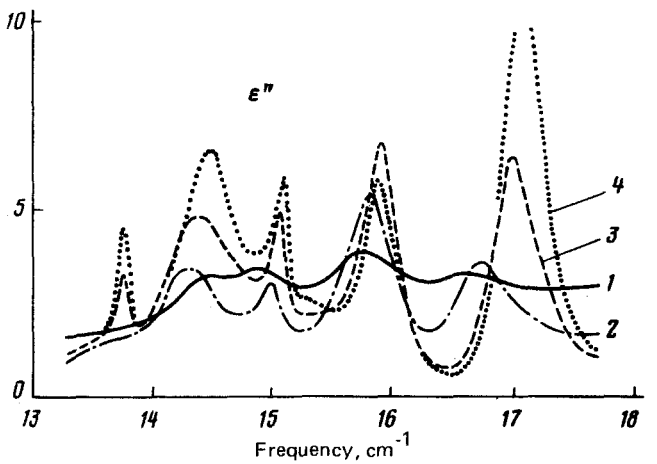

FIG. 2. Low-temperature spectra $\epsilon''(\nu)$ of $RbAg_4I_5$. 1–4—112, 47, 20, and 16 K, respectively.

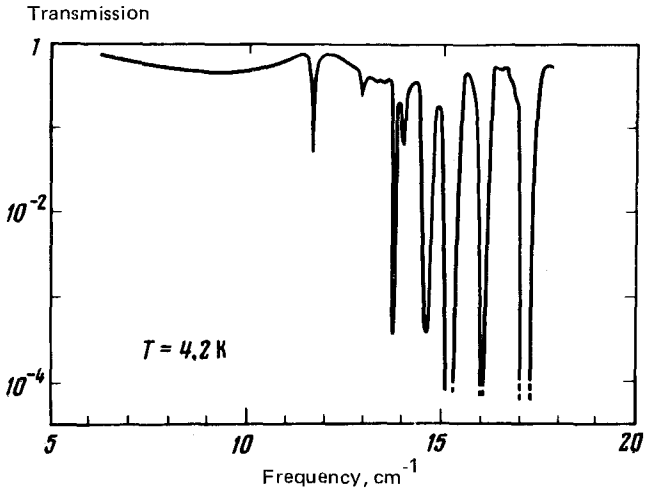

FIG. 3. Transmission spectra of 280-μm-thick $RbAg_4I_5$ plate at liquid-helium temperature.

duces the diffuse mobility of the Ag^+ ions. This process is accompanied by an increase in the Ag^+ lifetime at the local equilibrium positions, as can be seen in a narrowing of the 16-cm^{-1} mode upon cooling. We see from Fig. 1 that the changes which occur in the width and intensity of the line are not accompanied by a change in frequency. This result means that there is essentially no change in the local potential relief for the Ag^+ ions at the α-β transition.

At the transition to the γ phase the splitting of the mode is not accompanied by a change in the low-frequency value of ϵ' (Fig. 1); i.e., the resultant dielectric contribution of the various components is conserved. This result means that at least most of the lines resolved in the low-temperature phase appear simply because a degeneracy of the 16-cm^{-1} mode is lifted. It is also pertinent to note that the center of gravity of the split line remains near 16 cm^{-1}. Consequently, the elasticity of the Ag^+ potential changes only slightly again at the β-γ transition, and the sharp decrease in the conductivity results from a disruption of the diffusion paths for Ag^+ ions in the lattice.

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[1)]The samples in the γ phase were not put in a single domain.

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