"Phason" in the submillimeter spectrum of $CsCuCl_3$ single crystals

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A high *Q*, low-frequency mode resulting from phase fluctuations of the helicoid spatial modulation of the crystal's structure was observed in the spectrum of the low-temperature phase of a hexagonal $CsCuCl_3$ perovskite by using the submillimeter-spectroscopy method.

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A hexagonal $CsCuCl_3$ perovskite today is the only known material with a structural phase transition which leads to the formation of a helicoidally modulated structure in the low-temperature phase.[1] For the purpose of searching for excitations of the crystal lattice associated with this type of phase transitions, we investigate in this paper the dielectric spectra $\epsilon^* (\epsilon,T)$ of $CsCuCl_3$ crystals in the submillimeter wave range.

The $CsCuCl_3$ crystals were grown form an aqueous solution of cesium chloride

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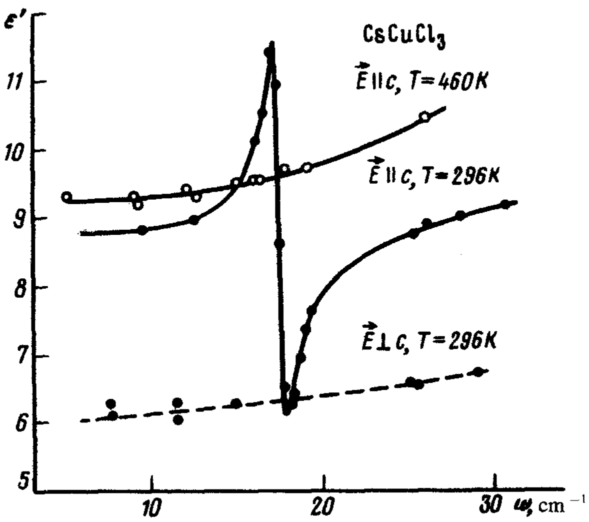

FIG. 1. Dependence of ϵ' on frequency.

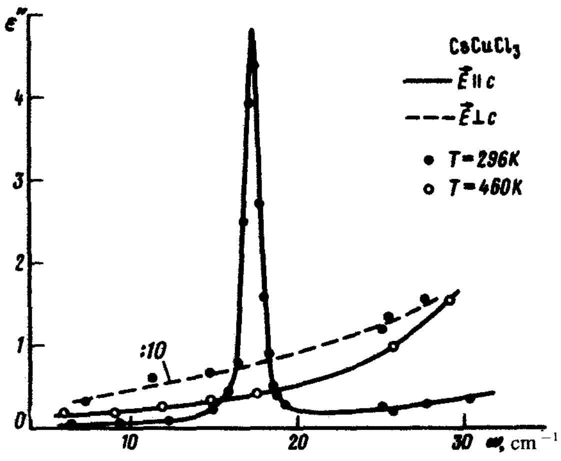

FIG. 2. Dependence of ϵ'' on frequency.

and copper chloride in a molar ratio of 1:2 by reducing the temperature in the range of 313–308 K and at pH = 3.5.

The measurements were performed with use of a submillimeter LOV spectrometer such as that in Ref. 2. The values to be measured were the modulus and phase of the transmission coefficient of the plane-parallel, X-cut plate of the investigated crystal under conditions of normal incidence of radiation.[3] The dielectric parameters of the sample were calculated on the basis of the relations for an infinite plane-parallel layer.

The resultant spectra of the real and imaginary parts of the dielectric constant are shown in Figs. 1 and 2. At E$\|c$ the spectrum exhibits a sharp line with an anomalously low frequency for lattice modes, which vanishes at $T > T = 423$ K. The observed line is described well by the oscillator formula:

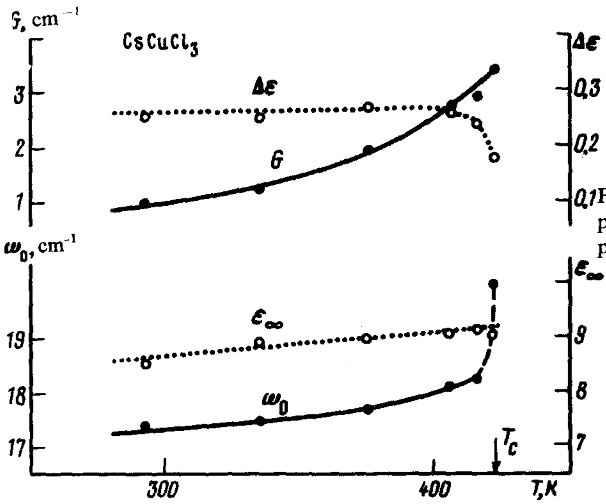

FIG. 3. Temperature dependences of the parameters of the resonance model of dispersion of the dielectric constant.

$$\epsilon(\omega) = \epsilon_\infty + \frac{\Delta\epsilon\,\omega_0^2}{\omega_0^2 - \omega^2 + i\omega\Gamma},$$

where ω_0, Γ, and $\Delta\epsilon$ are the natural frequency, damping, and the dielectric contribution of the oscillator, ϵ_∞ is the contribution of the higher frequency modes, and ω is the emission frequency. Their temperature dependences are shown in Fig. 3. The 3-kOe external magnetic field does not change the line parameters within the accuracy of the experiment.

To interpret the obtained results, we shall perform a short group-theoretical analysis of the far IR spectra of the $CsCuCl_3$ crystals. In the low-temperature region the crystal has a space group D_6^2 or its enantiomorphous group D_6^3; the primitive cell contains six formula units that form a helicoid chain along the c axis.[4] At $T = 423$ K we have a first-order phase transition to a more simple structure with two formula units in the primitive cell. The space symmetry group of this phase at present is ambiguous[5,6]; in analogy with the preceding theoretical work, we assume the transition $D_{6h}^4 \to D_6^2$.

The transition is noteworthy because the order parameter lies on the Δ line of the Brillouin zone $[k_c = (0,0,\xi)$ and $\xi = 2\pi/3c]$[1] and because it is a four-component parameter (representation in Kovalev notations[7]). If the complex components of the order parameter are denoted by η_1, η_1^*, η_2, and η_2^* [η_1 and η_2 at the point $(0,0,2\pi/3c)$ and η_1^* and η_2^* at the point $-(0,0,2\pi/3c)$] and a domain in which $\eta_{1s} = \eta_{1s}^*$ and $\eta_{2s} = \eta_{2s}^* = 0$ is chosen, then we can show that below T_0 the four-dimensional space of the eigenvector of the soft mode breaks down into three subspaces: an amplitudon (amplitude fluctuations of the modulation wave) with an eigenvector $\eta_1 + \eta_1^*$ and with a symmetry A_1, a phason (phase fluctuation wave) with a symmetry A_2, and a two-dimensional space (η_2, η_2^*) with a symmetry E_2 corresponding to fluctuations of the enantimorphous modulation that is frozen in another domain. The phason is active in the IR spectrum when $E \| c$, which is attributable to the invariant $(\eta_1^3 + \eta_2^3 - \eta_1^{*3})P_c$ in the thermodynamic potential; below T it gives a term of the type $\eta_{1s}^2(\eta_1 - \eta_1^*)P_c$ which describes a bilinear interaction of the phason with the modes that have dipole moments along the c axis. The oscillator strength due to this interaction is proportional in first approximation to η_{1s}^4. It follows from considerations analogous to those in Ref. 8 that the frequency of the phason ω_ϕ is $\sim\eta_{1s}$ and hence the phason's contribution to the dielectric constant $\phi_{\Delta\epsilon}$ is $\sim\eta_{1s}^2$.

We submit that the observed low-frequency mode is a phason, i.e., it is directly associated with the phase fluctuations of the helicoidally modulated structure. In particular, this is consistent with the disappearance of the mode in the high-temperature phase and its insensitivity to the magnetic field. The fact that the frequency of the phason does not decrease to zero as $T \to T_0$ and even increases slightly is attributable to the basic strength of the transition when the order parameter is almost independent of the temperature below T_0.[1] Thus, the thermodynamic relations ($\omega_\phi \sim \eta_{1s}$, $\Delta\epsilon \sim \eta_{1s}^2$) obtained above may be violated because of the increasing importance of the effects of higher order in η_{1s}.

It was quite unexpected that at $T \ll T_0$ the phason had a high Q. In fact, the transition in $CsCuCl_3$ is an order–disorder transition (Jahn–Teller type), and it would appear that the soft modes causing it should be diffusion type. For a definitive explanation of the dynamics of the phase transformation in $CsCuCl_3$, one must conduct an additional investigation of the spectra of Raman scattering of light and of the inelastic scattering of neutrons.

From the viewpoint of symmetry, the phase transition in the $CsCuCl_3$ crystal is the first concrete case of a nonferroelectric phase transition in nonpolar point groups, for which one of the components of the soft mode becomes active in the IR spectrum. The equitranslational transitions of this type were analyzed theoretically by Petzelt.[9]

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