Soft-mode splitting in a $TlGaSe_2$ crystal

A. A. Volkov, Yu. G. Goncharov, G. V. Kozlov, and R. M. Sardarly
Institute of General Physics, Academy of Sciences of the USSR

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Some unusual features have been observed in the lattice dynamics of the $TlGaSe_2$ crystal. Specifically, the soft mode splits in two well above the phase-transition temperature ($T_c = 107$ K). The temperature dependence of one of the two components is anomalous: Its frequency increases instead of decreasing as the temperature approaches T_c.

Recent studies of the vibrational IR spectra of the multilayer semiconductor crystal $TlGaSe_2$ have revealed many interesting properties in its lattice dynamics: structural phase transitions (at $T_1 \sim 120$ K and $T_2 = 107$ K), an intense IR-active soft mode, and indications of a ferroelectric behavior (below T_1) and of an incommensurate phase (between T_1 and T_2).[1] In this letter we report the observation of an unexpected new effect in $TlGaSe_2$: an unusual temperature dependence of the soft mode. As in Ref. 1, the experimental basis of the study consisted of data on the dispersion of the dielectric function of $TlGaSe_2$ obtained over the frequency interval 6–23 cm^{-1} with an Epsilon backward-wave-tube submillimeter spectrometer.

The first conclusion reached in a detailed study of the dielectric spectra of various $TlGaSe_2$ samples was that the picture of the lattice dynamics drawn in Ref. 1 for $TlGaSe_2$ is not the only one possible. We have observed some $TlGaSe_2$ samples which exhibit quite different properties.

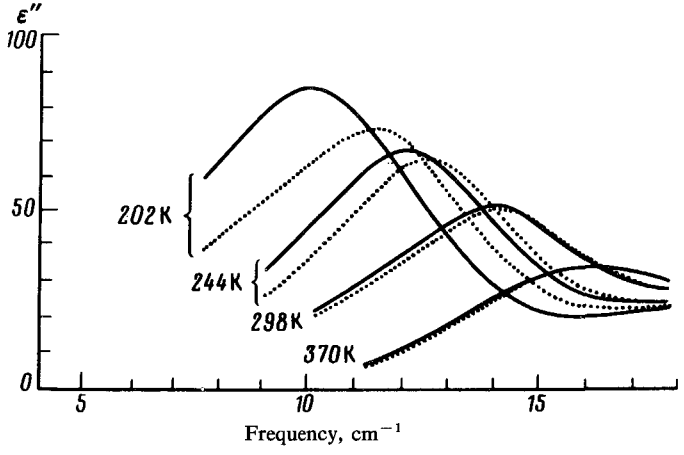

FIG. 1. The spectra $\epsilon''(\nu)$ of an "anomalous" $TlGaSe_2$ crystal for two mutually orthogonal orientations in the cleavage plane (solid and dotted curves). Solid curves—soft mode with the normal temperature dependence[1]; dotted curves—soft mode which splits into two components with a further decrease in the temperature (Fig. 2).

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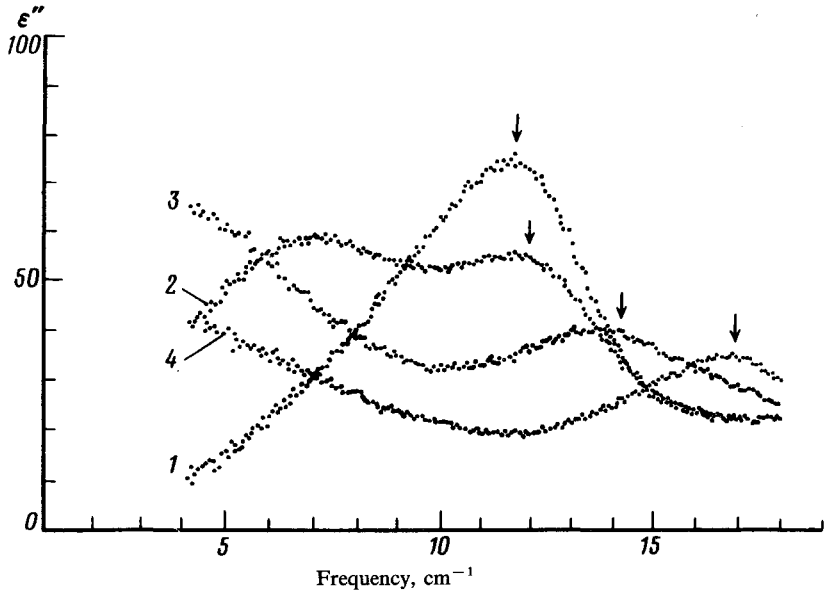

FIG. 2. Low-frequency spectra $\epsilon''(\nu)$ of an "anomalous" $TlGaSe_2$ crystal in one of the two orthogonal orientations. The arrows show that component of the soft mode which exhibits the anomalous temperature dependence. 1–202 K; 2–157 K; 3–138 K; 4–121 K.

Figure 1 shows the submillimeter spectra of the imaginary part of the dielectric function, $\epsilon''(\nu)$, one of these "anomalous" samples, for two orthogonal directions in the cleavage plane.[1)] Here we can clearly see the soft mode of the phase transition at T_2, which differs in no way from that observed previously[1] at room temperature and above. In terms of its dielectric properties, the crystal is essentially isotropic in the cleavage plane at room temperature.

As the sample is cooled we see indications of an anomalous behavior: The polarizational degeneracy of the soft mode is gradually lifted, and the vibrational spectra for the two orientations become different. Analysis of these spectra shows that in one of the orientations the behavior of the soft mode is the same as that in an ordinary isotropic sample.[1]

In the other orientation the soft mode evolves in a different way (Fig. 2). As the temperature is lowered, the soft mode begins to expand at a certain point, and then it splits into two components of roughly equal intensity (spectrum 2 in Fig. 2). The low-frequency branch is identical to the soft mode of the normal crystal, differing from it only in that its dielectric contribution is smaller by half.

The second, high-frequency, branch has an anomalous temperature dependence. Its frequency does not vary monotonically as the temperature is changed. Its frequency increases as the temperature approaches the transitions at T_1 and T_2 (Fig. 3).

These effects apparently stem from particular features of the multilayer structure of $TlGaSe_2$, specifically, the tendency of these crystals toward an interlayer disorder[2]

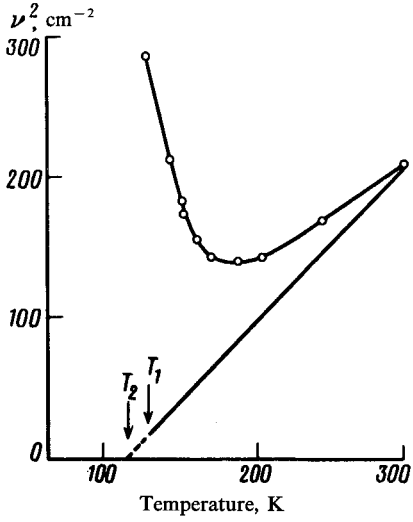

FIG. 3. Temperature dependence of the frequencies of the two components of the soft mode in an "anomalous" $TlGaSe_2$ crystal.

and the formation of polymorphic modifications.[3] The interlayer disorder, which is probably characteristic of most $TlGaSe_2$ samples, raises the symmetry of the crystal from C_{2h} to^2 C_{4h} and thus gives rise to a dielectric isotropy of $TlGaSe_2$ in the cleavage plane. The anomalous samples which we observed, on the other hand, are anisotropic and evidently have a lower symmetry. Their multilayer structure is thus at least partially ordered.

The multilayer structure of $TlGaSe_2$ can also explain the non-monotonic temperature dependence of the soft mode. The soft mode in $TlGaSe_2$ apparently interacts with other lattice vibrations, but this interaction is clearly different from the familiar interaction in which the role of soft mode is conveyed from one vibration to another in steps. In $TlGaSe_2$, as in a system with a long-wave structural modulation, this phenomenon may be complicated by the existence of additional couplings between lattice modes.[4] In particular, there may be coupled vibrations with different wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ satisfying $\mathbf{k}_1 - \mathbf{k}_2 = m\mathbf{q}$, where $\mathbf{q}$ is the wave vector of the lattice modulation, and m is an integer. Under these conditions we do not rule out the possibility that, as the vibration frequencies move closer together, one vibration will draw energy from the other, so that its frequency will increase.

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[1)]These directions cannot be definitely associated with crystallographic axes of the crystal because of the disorder of the multilayer structure of the crystal, as mentioned below.

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