Ferroelectric soft mode in the semiconductor crystal $TlGaSe_2$

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A study of the dispersion of the dielectric function in the crystal $TlGaSe_2$ has revealed some new, thermally unstable lattice excitations. These excitations suggest structural phase transitions in $TlGaSe_2$ at 107 K and, possibly, near 120 K.

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Research on the infrared and Raman spectra of $TlGaSe_2$ has frequently generated comments regarding the unusual behavior of the intensities of lines corresponding to lattice excitations in the temperature range 85–150 K (Refs. 1–3). It has been suggested that the unusual behavior of the spectra results from phase transitions in the crystal, which may involve its surface. No direct confirmation of this hypothesis has been found in the IR or Raman spectra.

In this letter we report a study of $TlGaSe_2$ at frequencies in the range 4–23 cm^{-1}, lower than those in Refs. 1–3, by submillimeter dielectric spectroscopy.[4] Using an Épsilon-2 backward-wave-tube spectrometer,[5] we recorded the frequency dependence of the real (ε') and imaginary (ε'') parts of the dielectric function of plane-parallel $TlGaSe_2$ samples over a broad temperature range, from room temperature down to 78 K. The samples were oriented in such a manner that the field **E** was parallel to the mounting plane (we observed no anisotropy of the dielectric properties of the crystal in this plane).

The experimental results are shown in Fig. 1. Some curves of $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$, which are easily distinguishable, are shown to illustrate the spectra actually recorded on the spectrometer. Curves 1–11 are numbered in accordance with the monotonic cooling of the crystal.

The most important results found from these spectra are as follows:

1. At frequencies $\nu \lesssim 20$ cm^{-1} there is an intense polar lattice oscillation of a resonance type in $TlGaSe_2$ with all the characteristics of a soft mode: As the temperature is lowered, its frequency (~ 14 cm^{-1} at room temperature) falls off, while the dielectric contribution increases (curves 1–4).

2. As mentioned in Refs. 2 and 3, the temperature region near 120 K is a special one for $TlGaSe_2$: As the crystal is being cooled, it is at these temperatures that the nature of the dielectric dispersion of the crystal begins to change from resonant to relaxational. The effect can be seen clearly in the spectra of $\varepsilon'(\nu)$ at frequencies ~ 7–10 cm^{-1}, where the signs of both ε' and its derivative with respect to the frequency change (curves 4–7).

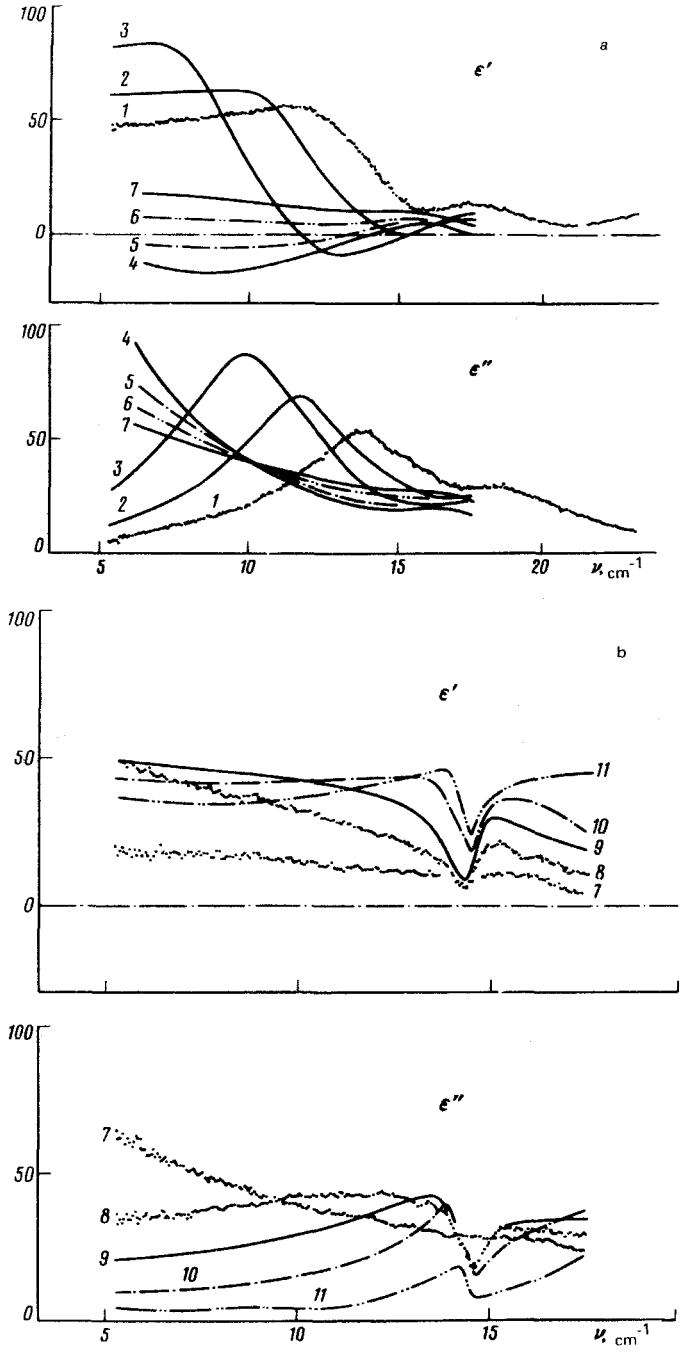

FIG. 1. Submillimeter dielectric spectra of $TlGaSe_2$ for various temperatures. 1–11—298, 244, 201, 123, 118, 113, 108, 106, 100, 94, and 78 K, respectively.

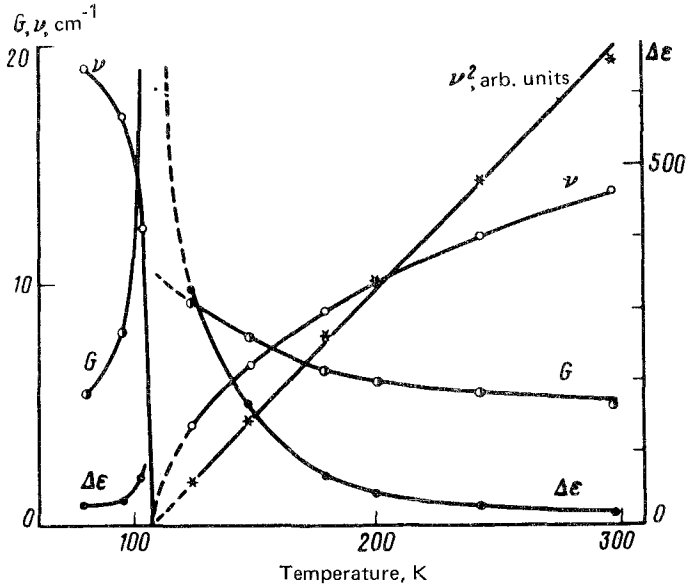

FIG. 2. Characteristics of the soft mode. ν, G, and $\Delta\varepsilon$: the frequency, damping, and dielectric contribution, respectively.

3. At 107 K the dynamic properties of $TlGaSe_2$ change abruptly (curves 7 and 8 in Fig. 1b). A new high-quality-factor absorption line appears at ~ 14 cm^{-1}, and the soft mode shifts very rapidly along the frequency scale from the microwave range to $\nu \sim 15$–20 cm^{-1} and decreases in intensity. As it goes through $\nu \sim 14$ cm^{-1}, it interferes with the hard lattice oscillation which has appeared here (the Fano effect[6]).

Figure 2 shows the temperature dependence of the characteristics of the soft mode according to least-squares calculations from the $\varepsilon'(\nu,T)$ and $\varepsilon''(\nu,T)$ spectra in a damped-oscillator model. It is clear from these results that we are dealing with a typical soft ferroelectric mode. The square of its frequency is a linear function of the temperature; the dielectric contribution $\Delta\varepsilon(T)$ exhibits an approximately Curie-Weiss temperature dependence with a constant $C = 5.5 \times 10^3$ K; and it exhibits a damping which depends comparatively weakly on the temperature. The point at which the mode frequency vanishes, according to an extrapolation of the $\nu^2(T)$ dependence, is 107 ± 2 K and thus coincident with the temperature of the sharp change in the spectra. All these results imply that a ferroelectric phase transition of the displacement type occurs at 107 K in $TlGaSe_2$.

In recording the curves of $\varepsilon'(T)$ and $\varepsilon''(T)$ we observed a thermal hysteresis $\Delta T \sim 0.5$ K at 107 K; the hysteresis suggests that this is a first-order transition. The same conclusion follows from an analysis of the behavior of the soft mode below 107 K: The frequency of this mode changes essentially abruptly near 107 K.

There is yet another important point to be noted with regard to the phase transition at 107 K. Judging from the change in the nature of the dielectric dispersion, from

resonant to relaxational, at ~ 120–107 K, what is happening at 107 K is apparently not a simple phase transition from the paraelectric to the ferroelectric phase. The appearance of relaxational excitations in crystals exhibiting displacive phase transitions is typical of ferroelectric crystals with incommensurate phases. We have observed a similar behavior in the dielectric properties of several other ferroelectrics [e.g., in thiourea,[7] $SC(NH_2)_2$]. By analogy, it may be suggested that in the case of $TlGaSe_2$ the transition to the ferroelectric phase at 107 K is preceded by a phase transition ($T \sim 120$ K) to a state with a spatially modulated structure and that, beginning at 120 K, we are observing a splitting of the soft mode into two components, one of which is a relaxational mode.

An attempt might also be made to interpret the appearance of a low-frequency relaxation as a central-peak effect.[8] Dielectric measurements in the microwave range and in the static case would appear to be important for a final resolution of this question.

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