Weak ferroelectricity in layered $A^3B^3C_2^6$ ferroelectric-semiconductor materials

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A phase transition to a phase which has a weak ferroelectricity has been observed for the first time in layered $TlInS_2$ and $TlGaSe_2$ ferroelectric-semiconductor materials. The detected phase transition is assumed to be an isomorphic phase transition.

Only several ferroelectric crystals, categorized as weak ferroelectrics in which an unusual temperature dependence of the spontaneous polarization has been observed, have so far been identified: $P_S(T)$ tends to zero with decreasing temperature and changes sign in the ferroelectric phase.[1] We are reporting here the experimental observation of a weak ferroelectricity in a new class of crystals—$A^3B^3C_2^6$ layered ferroelectric-semiconductor materials.

The layered semiconductors $TlInS_2$ and $TlGaSe_2$, which have the symmetry C_{2h}^6 at room temperature, sequentially undergo phase transitions to an incommensurate phase and a ferroelectric phase upon lowering the temperature ($T_i = 216$ K, $T_c = 201$ K and $T_i = 120$ K, $T_c = 110$ K, respectively).[2,3] The presence of a soft mode in $TlInS_2$ was reported in the experimental studies of the submillimeter dielectric spectra[4] and Raman spectra.[5] In addition, the interaction of two, hard, optical modes at 38 and 42 cm^{-1} has been observed in the study of Raman spectra of $TlInS_2$ at $T \simeq 75$ K.[6] It was shown in Ref. 7 that the soft mode in $TlGaSe_2$ far from the phase transition at high temperatures is split into two components, one of which is a soft mode and the other mode hardens as the temperature is lowered. It can thus be asserted that $TlInS_2$ and $TlGaSe_2$ have a soft mode and several hard, optical modes which interact with each other.

We have shown recently that a spontaneous polarization of $TlInS_2$ occurs as a result of the formation of two nonequivalent sublattices because of the nonequivalent atomic displacements which correspond to various instabilities of the crystal lattice.[8] This circumstance and the presence of interacting modes in these crystals have stimulated further studies of the insulating properties at low temperatures.

Low peaks $\epsilon(\Delta\epsilon \approx 1.5)$ have been detected at $T_{tr} = 79$ K and 64 K, respectively, on the temperature dependence of the dielectric constant of $TlInS_2$ and $TlGasSe_2$, which was measured along the polar axis (Figs. 1 and 2). Experimental studies of thermal hysteresis have shown that the maximum of ϵ is affected by hysteresis, $\Delta T = 2$ K, and hence is a first-order phase transition. The Curie–Weiss constant varies in the range $C \sim 2$–5, depending on the lots from which the crystals were taken. Application of a static field to the sample causes ϵ_{max} to be displaced up the temperature scale. In the saturated state the spontaneous polarization of the ferroelectric phase, upon lower-

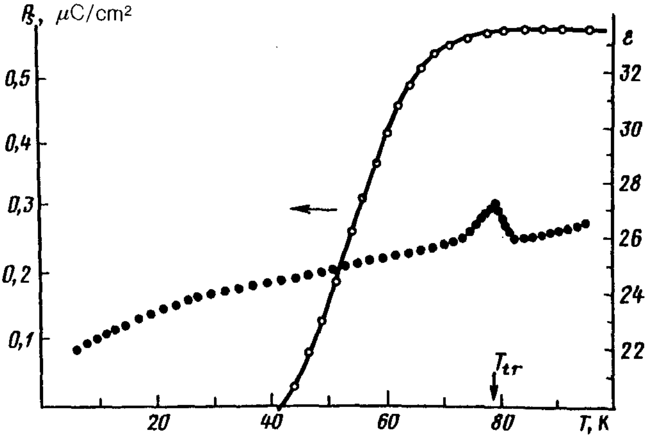

FIG. 1. Temperature dependence of ϵ' (●) at a frequency of 1 kHz and of P_s (○) at a frequency of 50 Hz of a $TlInS_2$ crystal.

ing the temperature, does not exhibit any anomalies near T_{tr} (Fig. 2). With a decrease in the temperature below T_{tr}, however, the spontaneous polarization decreases in absolute value to zero at $T_0 = 42$ K in the case of $TlInS_2$ and at $T_0 = 6$ K in the case of $TlGaSe_2$. The measurements of P_s along different crystallographic directions have shown that the spontaneous polarization changes only in the plane of the layer. It should be noted that $TlInS_2$ and $TlGaSe_2$ remain free of P_s and ϵ anisotropy below T_{tr} in the plane of the layer in the *a* and *b* directions. The phase transition at T_{tr} can be tentatively assumed to be isomorphic.

The few anomalies in $\epsilon(T)$, the Curie–Weiss constants, and the behavior of $P_s(T)$ below T_{tr} suggest that the low-temperature phase transition in $TlInS_2$ and

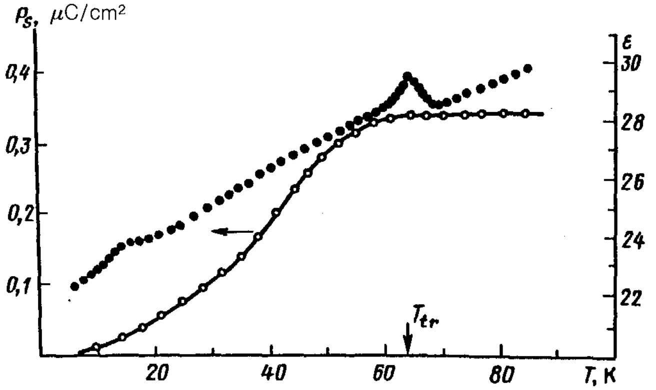

FIG. 2. Temperature dependence of ϵ' (●) at a frequency of 1 kHz and of P_s (○) at a frequency of 50 Hz of a $TlGaSe_2$ crystal.

$TlGaSe_2$ is a transition to a weak ferroelectric phase.[1] At small values of ϵ several modes in the low-temperature phase of these crystals can affect the background dielectric constant. In $TlInS_2$ we see that the soft mode with a frequency $\sim 23\ \mathrm{cm}^{-1}$, which corresponds to a transition to a ferroelectric phase, does not have a temperature dependence in this temperature range, while a harder mode, at $\sim 43\ \mathrm{cm}^{-1}$, exhibits a nearly square-root dependence at $T < T_{\mathrm{tr}}$ (Ref. 6). Taking into account the small value of the constant C, it can be concluded that the effective charges e_1 and e_2 of the soft mode and of the hard mode, which link P_s with their normal coordinates, in this case should be $e_1 \ll e_2$. According to the result obtained in Ref. 1, $P_s \to 0$ at $e_1 \ll e_2$ below the temperature at which the transition occurs in a weak ferroelectric. For $TlInS_2$ and $TlGaSe_2$ the functional dependences of P_s correspond to the values of the coefficient for a mixed invariant, $\delta > 0$.

The presence of a highly symmetric paramagnetic phase is a necessary condition for the existence of a weak ferroelectricity. The assumption that the paramagnetic phase is present in $A^3B^3C_2^6$ in this case is plausible.[9] In $TlGaSe_2$, for example, the monoclinic angle is 20′ (Ref. 10) and the transition from the paramagnetic phase to the paraelectric phase can be affected through a slight monoclinic distortion of the highly symmetric tetragonal lattice, D_{4h}.

The low-temperature phases in $TlInS_2$ and $TlGaSe_2$ thus qualify, in our view, as phases which have a weak ferroelectricity.

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