INVESTIGATION OF A NEW LINE OF PHASE TRANSITIONS IN TRIGLYCINE SELENATE AT HIGH PRESSURES BY DIFFERENTIAL THERMAL ANALYSIS

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Abstract

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INVESTIGATION OF A NEW LINE OF PHASE TRANSITIONS IN TRIGLYCINE SELENATE AT HIGH PRESSURES BY DIFFERENTIAL THERMAL ANALYSIS

(Presented by Academician L. F. Vereshchagin, April 29, 1967)

It is known that in a crystal of triglycine selenate $(NH_2CHCOOH)_3H_2SeO_4$, at atmospheric pressure, a second-order phase transition takes place with a Curie temperature of 22°C ([1,2]).

The ferroelectric properties of triglycine selenate (TGSe) crystals at high pressures were studied in works ([3,4]). In work ([4]), the curve of second-order phase transitions in a TGSe crystal was investigated at pressures up to 8000 kg/cm^2. It was found that, with increasing pressure, the Curie temperature shifts linearly into the region of higher temperatures. The value dT_K/dp is $+3.7 \cdot 10^{-3}$ deg/atm, which agrees with the result of work ([3]), obtained at pressures up to 2700 kg/cm^2.

In work ([4]), in electrical measurements in the pressure range from 6000 to 8000 kg/cm^2, a new line of phase transitions was discovered in the TGSe crystal; it was investigated in the temperature region $0 \div 50$°C. It was shown that this curve of equilibrium of two phases has a linear character.

The line of second-order phase transitions and the new line of phase transitions bound the region of existence of the ferroelectric state in the TGSe crystal.

To clarify the question of the nature of the newly discovered phase transformation in the TGSe crystal, we carried out the present investigation.

As is known, first-order phase transitions are accompanied by a jump-like change in the first derivatives of the thermodynamic potential: the volume V, entropy S, and enthalpy H, i.e., first-order transitions are accompanied by the release or absorption of latent heat of transition. The changes in these quantities during a first-order phase transition are related by the Clapeyron–Clausius equation

$$dT_K/dp = T\Delta V/\Delta H, \tag{1}$$

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

where T_{K} is the Curie temperature in °K; ΔV is the change in volume during the phase transition; ΔH is the change in enthalpy during the phase transition.

At high pressures, first-order phase transitions are recorded both by the jump in volume (piston-displacement method) ([6]) and by the thermal effect (differential thermal analysis method, d.t.a.) ([7,8]). We used the d.t.a. method.

One of the junctions of a differential copper–constantan thermocouple was placed in monocrystalline cerium, which was used as the reference substance for determining the sign of the thermal effect in TGSe during the phase transition, analogously to work ([8]). The readings of the differential thermocouple were recorded by a low-frequency thermographic recorder NTR-63 with photographic recording.

In the thermogram presented in Fig. 1, it is seen that the phase transition under study in TGSe is accompanied by a considerable thermal effect. This indicates that a first-order phase transition occurs here. The fact that the phase transitions in TGSe and cerium, located at different junctions of the differential thermocouple, produced peaks in opposite directions on the thermogram shows that the signs of the thermal effects of these phase transitions are the same.

As shown in work (7), the phase transition in metallic cerium, occurring at a temperature of 20°C and at a pressure of about 7500 kg/cm^2,

Fig. 1. Thermogram of the phase transition in triglycine selenate and cerium crystals at high pressures

Fig. 2. Phase p–T diagram of triglycine selenate. Points obtained: a–from temperature measurements of the dielectric permittivity; b–by the method of differential thermal analysis; v–from dielectric hysteresis loops

is accompanied by a positive thermal effect of 880±50 cal/g-atom. Consequently, the phase transition under study in TGSe is also accompanied by a positive thermal effect, i.e., by heat release, and hence by a decrease in enthalpy.

It is known that, under an isothermal increase of pressure, only phase transitions accompanied by a decrease in volume occur. Thus, in the Clapeyron–Clausius equation (1), for the phase transition under study in TGSe the quantities ΔV and ΔH are negative, T°K is positive, and therefore the quantity dT_k/dp is also positive, as is the case on the phase p–T diagram investigated in work (4).

To check the slope of the line of first-order phase transitions in the TGSe crystal, we recorded thermograms for various temperatures: +19°, +42.25°, +51.5°, +60.45°, +65°, and +70°C. The transition pressure was taken to be the pressure corresponding, on the thermogram, to the onset of the thermal effect. The pressure was measured with a manganin manometer with an accuracy of ±0.5%.

It was found (Fig. 2) that the slope of the line of first-order phase transitions in the TGSe crystal, determined by the DTA method, coincides with the analogous result obtained in work (4) by the method of electrical measurements. The value is

$$dT_k/dp = +32.8 \cdot 10^{-3} \text{ deg/atm}.$$

At the point with coordinates $p = 7500$ kg/cm^2 and $T = +49.6$°C, the line of first-order phase transitions meets the line of second-order phase transitions and continues above the meeting point with the same slope. The meeting point of the phase-transition lines in the TGSe crystal is a triple point; it separates the phases of the crystal that are in three different states.

In conclusion, we express our deep gratitude to the supervisor of the work, Academician L. F. Vereshchagin, as well as to B. A. Strukov and Yu. A. Pospelov, who took part in discussing the results.

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Note: Figure translations are in progress. See original paper for figures.