

Cooling-induced structural changes in proustite crystals

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A study of the kinetic characteristics of phase transitions in proustite shows that in this substance cooling induces structural changes which raise phase-transition temperatures. This effect stands in contrast with the ordinary retarding effect of cooling.

Proustite (Ag_3AsS_3) undergoes three phase transitions¹⁻³: to an incommensurate modulated structure at 60 K, to a commensurate modulated structure at 50 K, and to a ferroelectric phase at 28–30 K. It has been found that the ferroelectric phase transition has several distinctive kinetic features, which are manifested in particular in an inversion of the thermal-hysteresis loop recorded during a continuous change of the temperature.⁴

Cooling is ordinarily accompanied by a retardation of structural processes. The experimental results which we are reporting here show that in proustite cooling, as an inducing external agent, causes the temperatures of phase transitions to rise.

In the experiments we measure the temperature intervals of the various phase states of proustite for various crystal cooling rates, and we study the structural relaxation from the cooling-induced phase states at higher temperatures to equilibrium states. The temperature intervals of the phases are determined by an x-ray diffraction method, involving the changes in the diffraction intensity of a superstructural reflection of the incommensurate phase. Structural relaxation processes are detected from changes in the intensity of the superstructural reflection over time at a fixed temperature.

The samples are natural cleaved samples with dimensions of $2 \times 2 \times 0.02$ mm. The diameter of the working part of the thermocouple, positioned beside the sample, does not exceed 1 mm.

The order of experimental steps is as follows: The thermostatted volume of the cryostat holding the test sample is heated to some temperature above 60 K, held there in order to reach thermal equilibrium, and then cooled by blowing the vapor of gaseous helium (which serves as a coolant) through it. The rate of change of the temperature is adjusted by adjusting the coolant flow velocity. Structural relaxation can be observed in the cryostat by stopping the temperature change at the point of interest and holding the temperature constant within ± 0.1 K.

Figure 1 shows experimental results on the diffraction intensity of the superstructural reflection versus the temperature of the temperature-controlled volume for two crystal cooling rates. Curve I corresponds to a very slow temperature change ($\partial T / \partial t \approx 0$) and shows the temperature intervals of the equilibrium phases of proustite in the range 25–90 K. Curve II corresponds to a cooling rate $\partial T / \partial t = 6.8$ K/min. On

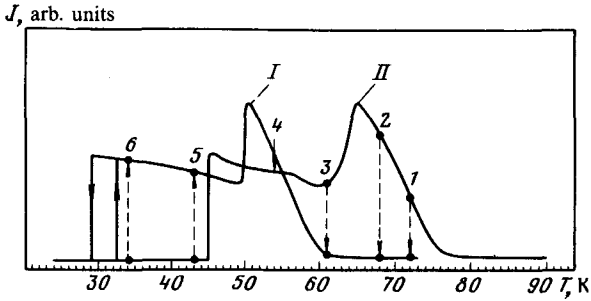


FIG. 1. The diffraction intensity of the superstructural reflection versus the temperature at various cooling rates: I— $\partial T/\partial t \approx 0$; II— $\partial T/\partial t = 6.8$ K/min.

these curves the temperature region of the transition from the incommensurate phase to the commensurate phase is marked by an abrupt decrease in the intensity, caused by a shift during the conversion of the superstructural reflection from the exact Bragg position. The temperatures of the boundaries of the high-temperature and ferroelectric phases, which are separated by an interval of modulated structures, are determined from the lowering of the diffraction intensity to the background level due to the absence of the superstructural reflection from these phases. A comparison of curves I and II clearly shows that the cooling raises the temperature of all three phase transitions of proustite. The results show that the shift of the transition temperatures away from their equilibrium values increases with increasing cooling rate.¹⁾

The structural states found during the cooling of the crystal and shown on curve II are metastable; when the crystal is held at a given temperature, they give way to the equilibrium states corresponding to curve I. Figure 2 shows the time evolution of the diffraction intensity of the superstructural reflection, giving us a picture of the structural relaxation processes at these transitions. The temperatures at which the relaxation processes are observed are shown by the arrows in Fig. 1. Curves 1 and 2 correspond to the inverse conversion from the cooling-induced incommensurate phase to

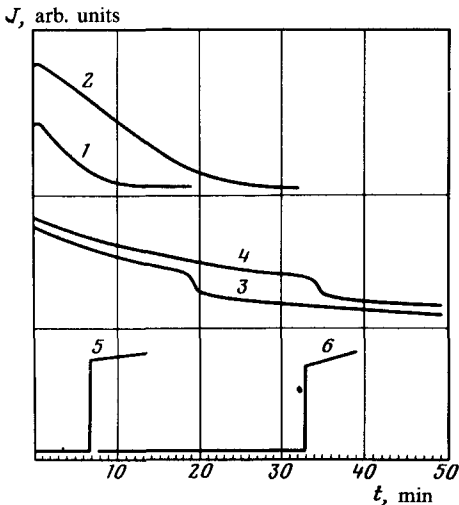


FIG. 2. Change in the intensity of the superstructural reflection during thermal stabilization at the following temperatures: 1—72 K; 2—68 K; 3—61 K; 4—54 K; 5—43 K; 6—34 K.

the equilibrium high-temperature phase. The process is quite smooth, and the relaxation time increases for a lower thermal-stabilization temperature. Curves 3 and 4 correspond to the inverse transition from the cooling-induced modulated phase to the equilibrium high-temperature phase for point 3 and to the equilibrium incommensurate phase for point 4. It should be noted that for these transitions there is no correspondence to a forward transition in the behavior of the intensity; in particular, the intensity has no peaks. Furthermore, the inverse transition from the commensurate phase to the incommensurate phase, like the forward transition, is accompanied by a decrease in the intensity, which implies a further shift of the superstructural reflection from the Bragg position and indicates that the crystallographic course of this conversion is irreversible. Curves 5 and 6 describe the inverse transition from the induced ferroelectric phase to the commensurate modulated phase. Here again we see an increase in the relaxation time with a decrease in the thermal-stabilization temperature. There is a difference from the processes described above, in that a new phase appears abruptly, reflecting the cooperative nature of ferroelectric transformations.

The slowness of the structural relaxation processes and the significant increase in the relaxation time with decreasing thermal-stabilization temperature indicate that the phase transitions in proustite are transitions of an ordering type. In this regard, the inducing effect of cooling consists of a stimulation of a reordering into low-temperature phases at higher temperatures, which is essentially equivalent to a supercooling of the ions which are becoming ordered with respect to the crystal lattice.

¹)Control experiments showed that the observed effects are not caused by any of the following: electric fields, stresses, a change in the defect composition of the crystal during cooling, or errors in the temperature measurements.

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