Temperature hysteresis and latent heat with a phase transition at 208 K in the superionic conductor $RbAg_4I_5$

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The temperature dependence of the heat capacity of $RbAg_4I_5$ single crystals near a phase transition at 208 K is investigated. In this transition the heat capacity and optical properties of the crystal exhibit hysteresis and the transition is accompanied by liberation of latent heat (70 cal/mole). On the basis of these results, it is concluded that the phase transition at 208 K in $RbAg_4I_5$ is a first-order transition.

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$RbAg_4I_5$ is a typical representative of a family of superionic conductors. This material has been studied in detail in recent years both on a purely scientific level, in

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connection with the investigation of the nature of the superionic state and phase transition mechanisms, as well as from the point of view of its possible applications in technology. Depending on the temperature of the surrounding medium, $RbAg_4I_5$ is found in one of three phases: α, β, γ.[1] Phases α and β are characterized by superionic conductivity, while the γ phase is not superionic. At $T\sim 122$ K there is a phase transition out of the γ phase into the β phase. This first-order transition is accompanied by a discontinuous change in the electrical conductivity by more than two orders of magnitude and it exhibits a temperature hysteresis.[2] A second transition (out of the superionic β phase into the superionic α phase) occurs at $T\sim 208$ K. Most researchers consider it to be a second-order phase transition. The smooth variation of the electrical conductivity in the vicinity of the transition,[3] as well as the possibility of describing the temperature variation of the heat capacity and the optical properties accompanying the transition with the help of the critical indices in the Ising model,[4,5] are usually given as experimental proof of such a transition. A number of researchers have pointed out evidence for a first-order phase transition.[6–8]

In this paper, we present experimental proof that the phase transition $\alpha \rightleftarrows \beta$ in $RbAg_4I_5$ is a first-order phase transition and is accompanied by a liberation of the latent heat and temperature hysteresis.

Single crystals for these investigations were grown by an isothermal method from an acetone solution of RbI and AgI.[9] The dimensions of the crystals attained are $\sim 10\times 12\times 8$ mm. Special cleaning methods and the technology used for growing the crystals allowed obtaining single crystals with the contamination by the main controlled impurities not exceeding 10^{-4} wt.%. The magnitude of the ionic conductivity, which is also a characteristic of the purity of $RbAg_4I_5$, was 0.30 $(\Omega\ \text{cm})^{-1}$ at 298 K. A differential thermal analysis (DTA) indicated the presence of a phase transition at 208 and 122 K and, in addition, at 122 K the DTA peak was ~ 2 times higher than the peak at 208 K.

The temperature dependence of the heat capacity in the vicinity of the phase transition ($\alpha \rightleftarrows \beta$) was investigated with a DSC-111 differential scanning calorimeter manufactured by the SETARAM company in the continuous temperature variation mode (the rate of change of the temperature was 1 K/min). The method essentially consists of comparing the parameters of the heat flows passing through two identical volumes, one of which contained the specimen being studied (in our case, in the form of one single crystal with weight ~ 0.4 g). The method is not an absolute method, so that the magnitudes of the heat capacities are determined to within a constant. Figure 1 shows the temperature dependences with heating and cooling. It is evident that within the region of the transition $\alpha \rightleftarrows \beta$ the heat capacity varies sharply in the temperature interval ~ 2 K. Comparing the dependences $C_p(T)$, obtained after cooling ($\alpha \rightarrow \beta$) and heating ($\beta \rightarrow \alpha$), it is evident that the position of the peaks in the heat capacity differs by approximately 3 K, which indicates the presence of temperature hysteresis. In making such a comparison, it is necessary to take into account the absolute error in the measurement of the temperature, which in the instrument used does not exceed ± 1 K (the error in measuring temperature differences on a single curve does not exceed ± 0.1 K). This indicates that all curves $C_p(T)$ can be shifted to the right or to the left along the temperature axis by not more than one degree and,

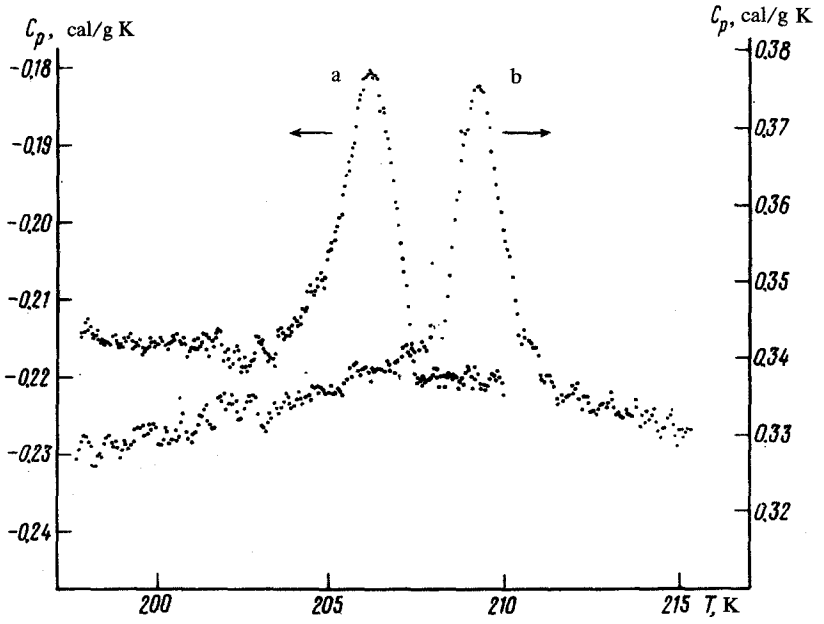

FIG. 1. Temperature dependence of the heat capacity of a single crystal of $RbAg_4I_5$ near the phase transition at 208 K. (a) After cooling; (b) after heating.

therefore, the width of the hysteresis ΔT is $(3 \pm 2)°$. It is natural to assume that within the limits of error indicated, the temperature after heating is too high, while after cooling it is too low. For this reason, we assume that the width of the temperature hysteresis of the heat capacity of $RbAg_4I_5$ accompanying the phase transition at 208 K lies in the range $1\ \text{K} < \Delta T < 3\ \text{K}$. The presence of such narrow peaks in the temperature dependence of the heat capacity (~ 2 K) as well as the existence of the temperature hysteresis allow us to assume that the transition $\alpha \rightleftarrows \beta$ is a first-order transition. From the curves $C_p(T)$, it is possible to estimate the latent heat of this transition $\Delta H = \int_{\Delta T} C_p(T)dT$. It was found to be equal to 55 cal/mole for the transition $\beta \rightarrow \alpha$ and 72 cal/mole for the transition $\alpha \rightarrow \beta$. The error in determining the absolute magnitude of ΔH did not exceed 30%.

An independent proof of the fact that in $RbAg_4I_5$ there is a first-order phase transition at 208 K is the temperature hysteresis discovered by us in the optical properties of the crystal. This experiment was performed as follows. A single-crystalline plate of $RbAg_4I_5$ with thickness ~ 0.4 mm was placed in an optical cryostat. A thin copper–constantan thermocouple, whose junction was in good thermal contact with the surface of the specimen, was attached to it. In this case, the thermocouple measured the temperature of the crystal at the point of contact. A temperature gradient of ~ 1 K/cm was created along the specimen. In such cases, when the temperature of the phase transition is attained, the entire crystal undergoes a phase transition to the new phase gradually rather than immediately. In addition, an interface forms and moves between the high- and low-temperature phases. Because of the difference between the optical properties of $RbAg_4I_5$ in the α and β phases, this interface is easily observed

with the help of a polarization microscope. Near the points of the transition $\alpha \rightleftarrows \beta$, we observed a sharp interface that separates the phases. As this interface passed through the point of contact of the thermocouple with the specimen, the temperature of the phase transition on the forward and backward hysteresis branches was recorded. The width of the hysteresis obtained in this manner was 1.0 ± 0.2 K, consistent with the result presented above.

These results uniquely indicate that the phase transition at 208 K in $RbAg_4I_5$ is a first-order transition with the temperature hysteresis $\Delta T \sim 1$ K and latent heat $\Delta H \sim 70$ cal/mole. It should be noted that our results contradict the data in Refs. 4 and 5, wherein a scaling behavior of the heat capacity and optical properties was observed near the phase transition at 208 K. The reason for this discrepancy may be attributable to the poor quality of the crystals studied in Refs. 4 and 5. It is well known that an inhomogeneity in the specimen (even within the scope of the self-consistent field) near the second-order phase-transition point leads to a scaling behavior of the heat capacity and optical properties of the specimen.[10] We assume that the qualitative conclusions in Ref. 10 can also be extended to a first-order phase transition, which could explain the results of the experiments in Refs. 4 and 5.

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