New low-temperature phase transitions in a superionic conductor $RbAg_4I_5$

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The temperature dependence of the submillimeter absorption spectra of a superionic conductor $RbAg_4I_5$ has been found to behave anomalously at 44 K and 30 K. This anomaly is interpreted in the context of the phenomenological Landau theory as a manifestation of the heretofore unknown structural phase transitions. It is suggested that at γ-phase temperatures ($T < 122$ K) several such transitions occur sequentially in $RbAg_4I_5$.

The $RbAg_4I_5$ crystal, which has a high ionic conductivity at $T > 122$ K ($\sigma \sim 0.3$ S/cm at $T \sim 300$ K), belongs to a group of substances which are now being studied extensively in an effort to determine the laws governing the ion transport in a solid.[1] We have recently reported the detection in $RbAg_4I_5$ of an unusual splitting of submillimeter IR spectra in the γ phase (at $T < T_2 = 122$ K) into a series of intense, high-Q ($\Delta\nu \sim 0.01$ cm^{-1} at $T = 4.2$ K) lines.[2] In the present letter we report the results of a comprehensive study of the formation of these lines. We found that at two temperature points the spectra behave in a peculiar way.

The measurements were carried out, as in the previous case,[2] by the method of the submillimeter backward-wave-tube spectroscopy[3] at frequencies ~ 10 cm^{-1}. The transmission spectra were recorded by passing a frequency-tunable monochromatic light through $RbAg_4I_5$ single-crystal wafers. Typical results are shown in Fig. 1. As the temperature is lowered, the absorption picture in $RbAg_4I_5$ changes appreciably: the absorption lines increase in intensity and become narrower. The important point, however, is that at $T_3 = 44$ K and $T_4 = 30$ K the spectra become enhanced by the new lines. This is clearly illustrated in Fig. 2, which is a plot of the temperature dependences of the frequencies of the lines that can be observed above the noise level. According to our initial data, the new lines appear not only at low frequencies but also at 20–30 cm^{-1}.

The results of the experiment may be viewed as evidence that phase transitions involving a change in the lattice symmetry occur in $RbAg_4I_5$ at the indicated points. Accordingly, let us theoretically determine whether low-temperature phase transitions can be achieved in $RbAg_4I_5$. It has recently been established that at atmospheric pressure this crystal has the following sequence of the phase transitions[4]:

$$P4_1 32\text{-}O^7(v)\ 208\ \mathrm{K}\ R322\text{-}D_3^7\,(v)\ 122\ \mathrm{K}\ P321\text{-}D_3^2\,(3v)\ ,$$

where v is the volume of the unit cell of the O^7 phase.

At $T_1 = 208$ K the phase transition is an equitransitional ferroelastic transition,

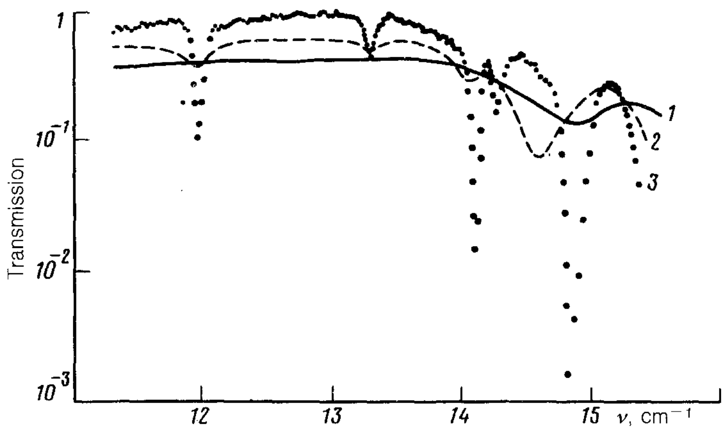

FIG. 1. Submillimeter transmission spectra of a 124-μm-thick, parallel-plate $RbAg_4I_5$ wafer obtained at several temperatures: 1—117 K; 2—36 K; 3—5 K. Spectrum 3—Actual recording of the spectrometer.

whose order parameter transforms according to a $3D$ $\tau_4(K_{12})$ representation of the O^7 group (the wave vectors and representations are indexed in accordance with Ref. 5).

The volume of the unit cell of the D_3^2 phase triples in the second phase transition ($T_2 = 122$ K). To describe this phase transition, we must therefore use a second order parameter, which in this case is an eight-component order parameter that transforms according to the $\tau_1(K_9)$ representation of the O^7 group. Such a system with two multicomponent order parameters can also have transitions to other phases which are different from D_3^7 and D_3^2.

To conclusively determine all the possible sequences of the phase transitions in $RbAg_4I_5$, we must begin with the thermodynamic potential which is constructed with allowance for invariants up to 16th degree in the components of the order parameter,

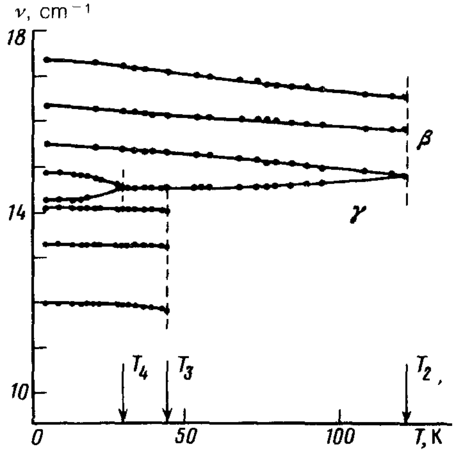

FIG. 2. Temperature dependences of the frequencies of the absorption lines detected in the transmission spectra (see Fig. 1). T_2—A known phase transition from the β phase to the γ phase.

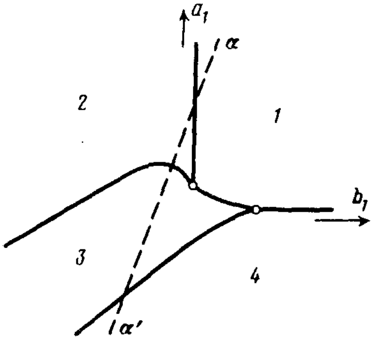

FIG. 3. Phase diagram of $RbAg_4I_5$. 1–4—$O^7(v)$, $D_3^7(v)$, $D_3^2(3v)$, and $O^7(27v)$ phases, respectively. $\alpha\alpha'$—Thermodynamic path.

since the minimum rational integral basis contains invariants of eighth degree. A potential of fourth degree can, however, be used in a simplified analysis, since the D_3^7 and D_3^2 phases observed experimentally correspond to single-parameter solutions. One such phase diagram of $RbAg_4I_5$ constructed in this manner is shown in Fig. 3. All lines on this diagram correspond to first-order phase transitions. If we assume that the phenomenological constants a_1 and b_1 (the coefficients of the quadratic terms in the potential) depend linearly on the temperature and pressure, the line $p = \text{const}$ (the temperature axis) in the a_1b_1 plane can be represented by a straight line. This line is drawn on the phase diagram in such a manner than the actually observed transition sequence, O^7–D_3^7–D_3^2, can be shown. We see that at low temperatures yet another phase transition, $D_3^2(3v)$–$O^7(27v)$, can occur. Furthermore, two-parameter T^4 phases, C_4^4, C_3^1, and C_2^3, can be "wedged in" between the one-parameter phases, D_3^2 and O^7, shown in the diagram. As a result, a series of phase transitions can occur at low temperatures. Consequently, the two points $T_3 = 44$ K and $T_4 = 30$ K observed by us probably do not constitute the full range of low-temperature phase transitions in $RbAg_4I_5$.

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