

# Raman spectra and structural phase transition in an $\text{Rb}_2\text{CdCl}_4$ crystal

A. D. Shefer, V. F. Shabanov, and K. S. Aleksandrov

*L. V. Kirenski Institute of Physics, Siberian Branch of the Academy of Sciences of the USSR, Krasnoyarsk*

(Submitted 20 December 1985; resubmitted 21 April 1986)

*Pis'ma Zh. Eksp. Teor. Fiz.* **43**, No. 10, 491–494 (25 May 1986)

The structural phase transition in a single-crystalline perovskite-type  $\text{Rb}_2\text{CdCl}_4$  is studied by the Raman-spectroscopy method. A “soft” lattice-vibration mode, which reconstructs the initial phase  $G_0$ , has been detected below the transition point.

A family of layered crystals with the general formula  $\text{A}_2\text{BX}_4$  or  $\text{ABX}_4$  [ $\text{KFeF}_4$ ,  $\text{RbFeF}_4$ ,  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ ,  $\text{TlAlF}_4$ , etc.] has a special place among the substances which have a promising future in various branches of electro-, magneto-, and acousto-optics and quantum electronics. These compounds have recently been studied extensively by various methods in order to determine their structural and dynamic characteristics. The general structure of such compounds is a framework of octahedral groups arranged in layers. The cations of metals or of organic complexes are situated in the voids between the layers.<sup>1-4</sup> The stability of structures of the type  $\text{ABX}_4$  and hence the dynamics of the phase transitions are governed by the mobility of the octahedral layers, as is the case in  $\text{CsFeF}_4$ ,  $\text{RbAlF}_4$ , and  $\text{TlAlF}_4$ , crystals,<sup>5-7</sup> in which the displacive transitions occur as a result of deviation of the axes of the octahedra relative to the axes of the crystal. On the other hand, the phase transitions in  $\text{A}_2\text{BX}_4$  [ $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ ] crystals are due primarily to the ordering processes.<sup>8</sup>

The  $\text{Rb}_2\text{CdCl}_4$  crystal which we have studied and which belongs to the  $\text{A}_2\text{BX}_4$  family is of interest because it does not have light cations which usually become ordered as a result of phase transitions of this sort.<sup>8</sup> Aleksandrov *et al.*<sup>9</sup> have shown that

at room temperature  $\text{Rb}_2\text{CdCl}_4$  has a  $14/mmm$  symmetry with two formula units in the unit cell. They have detected<sup>9</sup> at  $\sim 133$  K a phase transition in which the cell volume doubled in size. Analysis of experimental data has led them to conclude that the low-temperature phase ( $G_1$ ) of the crystal has a preferentially orthorhombic structure.

We have attempted to determine by the Raman scattering method the temperature-induced dynamic characteristics of the structure of an  $\text{Rb}_2\text{CdCl}_4$  crystal.

The experiment was carried out with use of an automatically controlled spectral apparatus which included an LG-106M laser, a DFS-24 spectrometer adapted for this purpose, an SM-3 computer, a set of KAMAK moduli, and a setup for visualizing the spectra (a graphic display, a plotting board). The use of a stack of individual program moduli generated by the RSX-11M operational system makes it possible to collect data and to control the experiment, to visualize the spectra in desired form, to analyze the spectra a second time, and to develop a permanent bank of spectra.<sup>10</sup>

The Raman spectra of the  $\text{Rb}_2\text{CdCl}_4$  crystal were obtained in all components of the Raman scattering tensor in each phase over the temperature interval 10–300 K. A helium cryostat, whose temperature was regulated within  $\pm 0.5$  K, was used in the low-temperature experiment. The measurements were carried out in a  $90^\circ$  geometry.

All the lattice vibration lines allowed by the selection rules were determined at room temperature (Fig. 1). Upon lowering the temperature to the phase-transition point, we saw in the spectrum no anomalous behavior in the frequencies or in the line intensities. Below the transition, the lines with a frequency of 46 or  $85\text{ cm}^{-1}$  begin to split into two components. One of the components is seen in the ( $yz$ ) polarization and the other component is seen in the ( $xy$ ) polarization. This splitting increases with decreasing temperature (Fig. 2), reaching 14 and  $18\text{ cm}^{-1}$ , respectively, at  $T = 10$  K.

Our group-theoretical analysis of the vibrational modes in each phase,  $G_0$  and  $G_1$ , has led to the following irreducible representations in the Raman scattering:

$$\Gamma(G_0) = 2A_{1g} + 2E_g; \quad \Gamma(G_1) = 5A_g + 3B_{1g} + 4B_{2g} + 6B_{3g}.$$

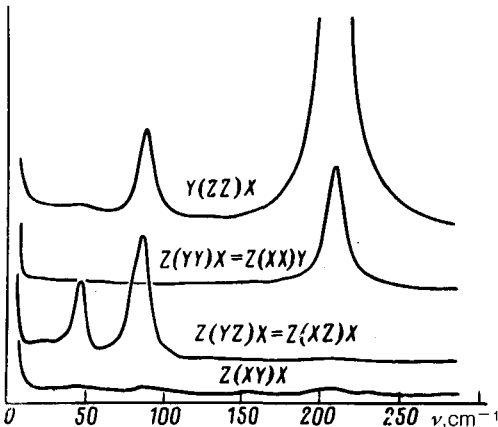


FIG. 1. The total spectrum of the  $\text{Rb}_2\text{CdCl}_4$  crystal at room temperature.

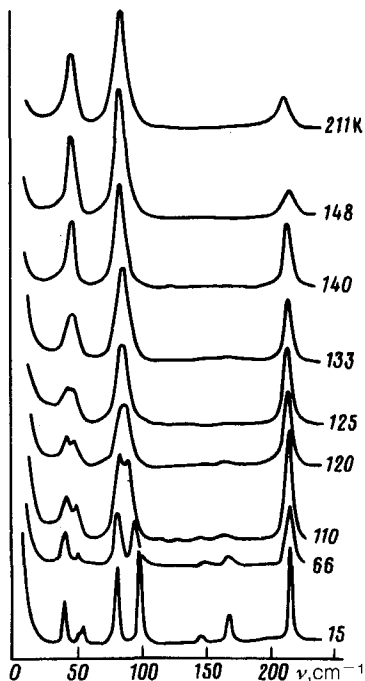


FIG. 2. The Raman spectrum of the  $\text{Rb}_2\text{CdCl}_4$  crystal in the  $z(yz + xz)x$  polarization at various temperatures.

According to the Raman-scattering tensor of the orthorhombic crystals,<sup>11</sup> the split-component modes have  $B_{3g}$  and  $B_{2g}$  symmetry. The splitting which is determined experimentally occurs due to the lifting of the degeneracy of the  $E_g$  vibrations as a result of a phase transition  $G_0 \rightarrow G_1$ .

An important feature can be seen in the spectrum of the diagonal ( $zz$ ) component (Fig. 3). Below the phase-transition point a line  $\nu_s$  extends from the wing of the Rayleigh scattering line. The frequency of this line increases anomalously with increasing distance from the phase-transition point. The behavior of the square of the frequency of this line shows that the temperature dependence is linear in the neighborhood of the phase transition, which is typical of a "soft" mode. A group-theoretical analysis of the motion in the  $G_1$  phase shows that both the Rb and Cl ions participate in the completely symmetric lattice vibrations. Consequently, the soft mode  $\nu_s$  is caused by the Rb and Cl sublattice vibrations. Since the phase transition involves a change in the volume of the unit cell, the soft mode must be caused by the condensation of the phonon from the boundary of the Brillouin zone.

It is interesting to note the large width of all the lines ( $6\text{--}10\text{ cm}^{-1}$ ) in the spectrum of not only the  $G_0$  phase but also the  $G_1$  phase over a broad temperature interval (up to 50 K). This feature, in our view, indicates that the amplitudes of thermal vibrations of the atoms which are displaced in the  $G_0 \rightarrow G_1$  transition are anomalously large in  $\text{Rb}_2\text{CdCl}_4$  in the  $G_1$  phase, as in several other similar crystals<sup>12</sup> that undergo phase transitions. The  $G_1$  phase acquires a constant component of the angle of rotation

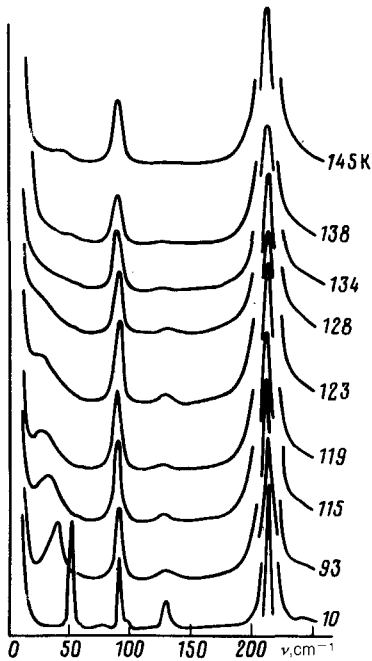


FIG. 3. The temperature dependence of the Raman spectrum in the  $y(zz)x$  polarization ( $\nu_s = 52 \text{ cm}^{-1}$  at  $T = 10 \text{ K}$ ).

of the octahedra, which corresponds to the increase in the order parameter and  $\nu_s(T)$ , and the thermal motion of the atoms relative to their new equilibrium positions is “frozen out” gradually as the temperature is lowered. For this reason, the  $G_1$  phase is still in a partially disordered state, so that a second phase transition at lower temperatures should not be ruled out.

In summary, the phase transition which we have studied in  $\text{Rb}_2\text{CdCl}_4$ , in contrast with crystals of the same structure with large molecular cations,<sup>8</sup> is preferentially a displacive transition with a clearly defined soft lattice-vibration mode in the low-temperature phase.

<sup>1</sup>M. Hidaka, B. J. Garrard, and B. M. R. Wanklyn, *Solid State Phys.* **12**, 2737 (1979).

<sup>2</sup>R. Kind, S. Plesko, and J. Roos, *Phys. Stat. Sol.* **a47**, 233 (1978).

<sup>3</sup>A. Leble, J. J. Pousseau, J. C. Fayet, J. Pannetier, J. L. Fourquet, and R. Pape, *Phys. Stat. Sol.* **a69**, 249 (1982).

<sup>4</sup>M. Couzi, P. L. Loyzance, R. Mokhlisse, A. Bulou, and J. L. Fouquet, *Ber. Buns. Phys. Chem.* **87**, 232 (1983).

<sup>5</sup>M. Hidaka, I. G. Wood, and F. R. Wondre, *Solid State Phys.* **12**, 4179 (1979).

<sup>6</sup>W. Kleeman, F. J. Schäfer, and J. Nouet, *Solid State Phys.* **15**, 197 (1982).

<sup>7</sup>K. S. Aleksandrov, B. V. Beznosikov, and S. V. Misyul', Preprint No. 333F, Institute of Physics, Siberian Branch, Academy of Sciences of the USSR, Krasnoyarsk, 1985.

<sup>8</sup>J. Petzelt, *J. Phys. Chem. Solids* **36**, 1005 (1975).

<sup>9</sup>K. S. Aleksandrov, L. S. Emelyanova, S. V. Misjul, and I. T. Kokov, *Solid State Commun.* **53**, 835 (1985).

<sup>10</sup>M. G. Mal'bin and B. A. Kravtsov, Preprint No. 334F, Institute of Physics, Siberian Branch, Academy of Sciences of the USSR, Krasnoyarsk, 1985.

<sup>11</sup>H. Poulet and J. P. Mathieu, *Vibrational Spectra and Symmetry of Crystals*, Gordon and Breach, Paris,

1970 (Russ. transl., Mir, Moscow, 1973).

<sup>12</sup>I. P. Makarova, S. V. Misjul, L. A. Muradyan, A. F. Bovina, V. I. Simonov, and K. S. Aleksandrov, Anharmonic Thermal Atomic Vibrations in the Cubic Phase of  $\text{Cs}_2\text{NaNdCl}_6$  Single Crystals, *Phys. Stat. Sol.* **b121**, 481 (1984).

*Translated by S. J. Amoretty*