

## LATTICE DYNAMICS AND PHASE TRANSITIONS

# Low-Temperature Specific Heat of the $\text{Rb}_2\text{KScF}_6$ Elpasolite

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**Abstract**—The specific heat of single-crystal  $\text{Rb}_2\text{KScF}_6$  is measured using ac calorimetry in the range 4–280 K. The results are discussed in the context of a group-theoretical analysis of possible distortions of the elpasolite structure and of experimental data obtained earlier with an adiabatic calorimeter in a narrower temperature region. © 2003 MAIK “Nauka/Interperiodica”.

Space group  $Fm\bar{3}m (O_h^5)$  is characteristic of several families of perovskite-like crystals, for instance, of those with the structure of elpasolite, cryolite, ordered  $\text{ReO}_3$ , and antiferite. The rich variety of possible distortions in these structures is one of the factors accounting for the existence of sequences of phase transitions which may result from changes in temperature, pressure, and/or atomic substitutions [1]. As the temperature is lowered, the original  $G_0$  structure undergoes consecutive distortions, which are usually accompanied by a gradual lowering of the symmetry.

A comprehensive group-theoretical and symmetry analysis of vibration representations in crystals with space group  $Fm\bar{3}m (O_h^5)$  was reported in [2–4]. The  $G_0$  structure, which is characteristic, in particular, of the elpasolites with a general formula  $A_2BB'X_6$ , was treated as being made up of rigid octahedral ionic groups  $B'X_6$  and  $A^+$  and  $B^+$  ions. The  $B'X_6$  octahedra are more rigid structural elements than  $BX_6$  because of the large difference in charge between the  $B$  and  $B'$  ions. It was established that the structures of distorted elpasolite phases may be considered as resulting from either simple rotations of the octahedra by a small angle about one of the fourfold axes of the unit cell or from a superposition of these rotations about several axes. One may conceive of situations for which rotations of the octahedra are accompanied by displacements of the  $A^+$  ion.

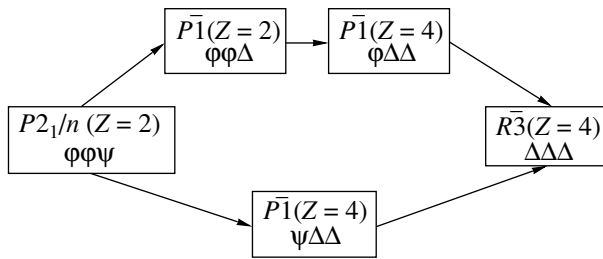
Possible combinations of two basic octahedron rotations,  $\varphi$  and  $\psi$ , were considered in [2–4]. In the first case, the octahedra in adjacent layers are rotated in opposite directions, and in the second case, in the same sense. Translational symmetry is changed only in the case of rotations of the  $\psi$  type. Complex combinations of simultaneous rotations of the same octahedra,  $\Delta = \varphi \pm \psi$ , were also found to be possible. Nineteen combinations of rotations corresponding to thirteen types of

space groups were analyzed altogether. The lowest symmetry of a distorted elpasolite structure was found to be triclinic ( $P\bar{1}$ ). However, the limiting case of superposition of rotations corresponds to trigonal symmetry (space group  $R\bar{3}$ ) when rotations of the type  $(\Delta\Delta\Delta)$  are involved.

Structural studies of a large number of halogen-containing elpasolites with atomic cations, in which sequential or single displacive-type phase transitions can occur, showed their lowest symmetry to be monoclinic ( $P2_1/n$ ,  $\varphi\varphi\psi$  rotations) [1]. However, since most crystals have not been studied below 70–100 K, one cannot exclude the possibility that their structure undergoes a more complex distortion as the temperature is lowered further.

One such crystal is the  $\text{Rb}_2\text{KScF}_6$  elpasolite. Optical, thermophysical, and structural studies carried out in the temperature region  $100 < T < 310$  K revealed that this crystal undergoes two sequential phase transitions:  $Fm\bar{3}m (G_0) \rightarrow I4/m (G_1) \rightarrow P2_1/n (G_2)$  [5]. In accordance with the entropy changes occurring at the temperatures  $T_1 = 252.4$  K and  $T_2 = 222.8$  K, both structural transformations were assigned to displacive phase transitions. We note that Raman investigations showed the octahedra to remain regular (rigid) structural elements in both the cubic and distorted phases of  $\text{Rb}_2\text{KScF}_6$  [1, 6]. This experimental conclusion permits one to consider that structural distortions in the tetragonal and monoclinic phases are connected only with octahedron rotations of the type  $(000) \rightarrow (00\varphi) \rightarrow (\varphi\varphi\psi)$ .

In accordance with [2–4], the phase alteration sequence observed in the  $\text{Rb}_2\text{KScF}_6$  crystal [5] could be continued below 100 K along two paths (Fig. 1); in other words, one could conceive, besides the known phase transitions, of two or three additional phase trans-



**Fig. 1.** Possible paths of further distortion of the monoclinic phase of crystals with elpasolite structure [2–4].

formations. The low-temperature phase was found to be triclinic in related ammonium-based  $(\text{NH}_4)_2\text{NH}_4M^3+\text{F}_6$  crystals ( $M^{3+} = \text{Ga}, \text{Sc}$ ) [7, 8] as a result of phase-transition-induced ordering of the octahedral and tetrahedral ionic groups. Note that all the phase transformations depicted schematically in Fig. 1 are clearly pronounced first-order transitions, because the number of components of the distortion that was already present in the  $G_{i-1}$  phase changes in the  $G_i$  phase.

Calorimetry is the most convenient method of searching for new phase transitions, because it reliably detects heat capacity anomalies caused by transformations of any nature. This stimulated our present measurements of the specific heat of  $\text{Rb}_2\text{KScF}_6$  in the temperature interval 4–280 K by using a calorimetric technique based on alternating heat current (ac calorimeter). The goals of the study were as follows: (i) to search for heat capacity anomalies at temperatures below 100 K, which could be associated with a possible further symmetry lowering, and (ii) to analyze the results, taking account of the earlier data obtained by using adiabatic calorimetry, in order to find whether inclusion of the low-temperature specific heat affects the earlier determined entropy associated with phase transitions.

The sample was prepared in two stages. First,  $\text{Rb}_2\text{KScF}_6$  was synthesized from a melt of corresponding amounts of the anhydrous starting components  $\text{RbF}$ ,  $\text{KF}$ , and  $\text{ScF}_3$  in a graphite crucible in an argon environment. Next, a transparent, colorless  $\text{Rb}_2\text{KScF}_6$  single crystal was grown using the Bridgman method in an evacuated and sealed platinum ampule. X-ray studies carried out at room temperature (in the cubic phase) showed the single crystal thus prepared to contain no foreign phases.

Dynamic measurements of the  $\text{Rb}_2\text{KScF}_6$  specific heat were performed in the range 4–280 K on a modified Sinku Riko ACC-1VL calorimeter. The sample for study, cut from a bulk single crystal, was a plane-parallel platelet measuring  $2 \times 2 \times 0.2$  mm. The light beam emitted by a stabilized halogen lamp was chopped and, on passing through an optical waveguide, produced a periodic variation of the sample temperature within a

few millikelvins. The temperature oscillations were detected with a differential chromel–alumel thermocouple made of wires 0.025 mm in diameter, whose junctions were fixed to the sample and the surrounding copper block with GE7031 varnish. Gaseous helium filling the measurement cell at a low pressure (10 mbar) provided heat removal from the sample to the copper block. The absolute value of the temperature of the block was determined with a platinum and a germanium resistance thermometer. The temperature of the sample was slightly higher than that of the copper block and was found as  $T_B + \Delta T_{DC}$ , where  $T_B$  is the temperature of the copper block measured with the resistance thermometer and  $\Delta T_{DC}$  is the constant component of the temperature difference measured by the thermocouple.

There is a frequency range with characteristic time short as compared with the relaxation time of the sample temperature to the copper block temperature, but long as compared with the internal relaxation time. With appropriate excitation frequencies, the specific heat is inversely proportional to the amplitude of temperature oscillations  $\Delta T_{AC}$  measured with the differential thermocouple. Measurements at different temperatures were made at frequencies from 2 to 20 Hz, with the larger frequency values lying in the low-temperature region. The temperature variation rates chosen in the heating and cooling runs were 10 to 30 K/h. The sample temperature was corrected taking the corresponding value of  $\Delta T_{DC}$  into account.

These measurements yielded relative values of the specific heat, which were reduced to absolute values by comparing the specific heat obtained at 200 K with that measured by us earlier using adiabatic calorimetry [5]. Above and below this temperature, the specific heat measured with the latter method was found to be slightly larger. This difference reaches its largest value, 1%, at 110 and 275 K.

The temperature dependence of the specific heat of elpasolite  $\text{Rb}_2\text{KScF}_6$  measured using the dynamic method is presented graphically in Fig. 2. In the region 4–100 K, which has not been covered previously in adiabatic-calorimetry measurements, no specific-heat anomalies were detected beyond the experimental scatter. This implies that no structural transformations with an enthalpy greater than 0.5 J/mol occur in this temperature region. Thus, the monoclinic phase of the  $\text{Rb}_2\text{KScF}_6$  elpasolite remains stable down to very low temperatures, at least to 4 K.

It appears of interest to compare our observations with the recent nonempirical calculations of the static and dynamic properties of  $\text{Rb}_2\text{KScF}_6$  in the three phases [9]. The results of the first-principles calculations made within a microscopic ionic-crystal model which takes into account the deformability and polarizability of ions are in qualitative agreement with experimental data related to the determination of the unit-cell parameters, angles of rotation of the octahedra, and

phase transition temperatures. Calculations of the total lattice vibration spectrum revealed the existence of unstable vibrational modes in the cubic and tetragonal phases of  $\text{Rb}_2\text{KScF}_6$ ; these modes condense at the center and edge of the Brillouin zone, respectively. As for the monoclinic phase, no unstable modes were found in its vibration spectrum, because, in accordance with the above calculations, transitions to lower symmetry phases in  $\text{Rb}_2\text{KScF}_6$  are impossible because the  $P2_1/n$  phase is stable down to 0 K.

As expected from the study of  $\text{Rb}_2\text{KScF}_6$  using adiabatic calorimetry [5], our calorimetric measurements made above 100 K revealed two anomalies in the specific heat, which are in agreement with the known phase transitions between the cubic, tetragonal, and monoclinic phases. The temperatures of the maxima in the specific heat,  $T_1 = 253.4 \pm 0.2$  K and  $T_2 = 224.9 \pm 0.2$  K, differ from the values  $T_1 = 252.4 \pm 0.1$  K and  $T_2 = 222.8 \pm 0.1$  K found using adiabatic calorimetry [5]. Note that the samples used in the present measurements and in [5] were cut from different single crystals. It is known [1] that the phase transition temperatures determined in different samples of fluorine-containing perovskite-like crystals, including the elpasolites, can differ by up to 5–7 K.

The change in enthalpy at a first-order phase transition (latent heat) cannot be measured using the above method of ac calorimetry; as a result, the shape of the specific-heat peak derived in this experiment may differ from that found from adiabatic measurements. Indeed, as seen from Fig. 2, the maximum value of the specific heat at  $T_2$  (which corresponds to a first-order phase transition to the monoclinic phase [5]) is 260 J/mol K; this value is substantially below the value ( $\geq 310$  J/mol K) found using adiabatic calorimetry [5]. This difference becomes particularly noticeable when comparing the excess specific heats, whose determination requires evaluation of the lattice contribution.

The lattice specific heat was determined by fitting the Debye and Einstein functions,  $C_L(T) = A_1 D(\Theta_D/T) + A_2 E(\Theta_E/T)$ , to the experimental values of the specific heat measured at a sufficient distance from  $T_1$  and  $T_2$ . The  $C_L(T)$  expression chosen describes the temperature dependence of the experimental specific heat satisfactorily. Within the temperature region 4–110 K, the average deviation does not exceed 1%. Varying the temperature interval that corresponds to the phase transition region and is excluded from the fitting procedure from 110–270 to 140–270 K did not bring about marked changes in the parameters  $\Theta_D$  and  $\Theta_E$ ; these parameters were found to be 148.5 and 335.5 K, respectively. Because the excess specific heats associated with the high- and low-temperature phase transitions overlap in the region between  $T_1$  and  $T_2$  (Fig. 2), we determined the excess thermodynamic functions corresponding to the phase transition sequence  $G_0 \rightarrow G_1 \rightarrow G_2$ . Inte-

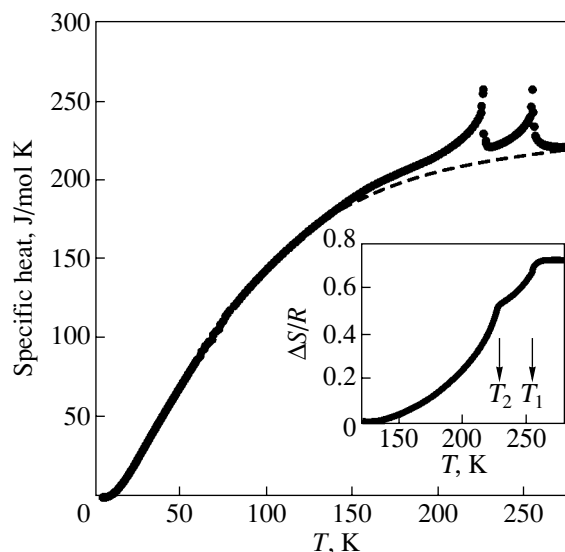


Fig. 2. Temperature dependence of the specific heat of a  $\text{Rb}_2\text{KScF}_6$  crystal. Dashed line is the lattice specific heat. Inset: temperature dependence of the excess entropy.

gration of the  $\Delta C_p(T)$  and  $(\Delta C_p/T)(T)$  functions yielded values of the enthalpy  $\Sigma \Delta H_i = \Delta H_1 + \Delta H_2 = 1250 \pm 70$  J mol<sup>-1</sup> and of the entropy  $\Sigma \Delta S_i = \Delta S_1 + \Delta S_2 = 6.0 \pm 0.3$  J (mol K)<sup>-1</sup>. The temperature dependence of the dimensionless excess entropy  $\Delta S/R$  is shown graphically in the inset to Fig. 2; its value at saturation (0.73) is in good agreement with that derived in the adiabatic calorimeter experiments (0.71) [5].

Thus, our present studies and the analysis of the low-temperature specific heat of the  $\text{Rb}_2\text{KScF}_6$  elpasolite, considered together with the data from [5, 9], show that the monoclinic phase of this crystal remains stable down to 0 K and that allowance for the data on the  $C_p(T)$  relation below 100 K does not influence the accuracy with which the thermodynamic functions of the sequential phase transitions in this crystal are determined.

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## REFERENCES

1. I. N. Flerov, M. V. Gorev, K. S. Aleksandrov, *et al.*, *Mater. Sci. Eng. R* **24** (3), 81 (1998).

2. S. V. Misyul', *Kristallografiya* **29**, 941 (1984) [*Sov. Phys. Crystallogr.* **29**, 554 (1984)].
3. K. S. Aleksandrov and S. V. Misyul', *Kristallografiya* **26**, 1074 (1981) [*Sov. Phys. Crystallogr.* **26**, 612 (1981)].
4. M. Couzi, S. Khaïroun, and T. Tressaud, *Phys. Status Solidi A* **98** (2), 423 (1986).
5. I. N. Flerov, M. V. Gorev, S. V. Mel'nikova, *et al.*, *Fiz. Tverd. Tela (St. Petersburg)* **34** (7), 2185 (1992) [*Sov. Phys. Solid State* **34**, 1168 (1992)].
6. A. N. Vtyurin, A. Bulou, A. S. Krylov, and V. N. Voronov, *Fiz. Tverd. Tela (St. Petersburg)* **43** (11), 2066 (2001) [*Phys. Solid State* **43**, 2154 (2001)].
7. S. V. Mel'nikova, S. V. Misyul', A. F. Bovina, and M. L. Afanas'eva, *Fiz. Tverd. Tela (St. Petersburg)* **42** (2), 336 (2000) [*Phys. Solid State* **42**, 345 (2000)].
8. M. V. Gorev, I. N. Flerov, S. V. Mel'nikova, *et al.*, *Izv. Ross. Akad. Nauk, Ser. Fiz.* **64** (6), 1104 (2000).
9. V. I. Zinenko and N. G. Zamkova, *Fiz. Tverd. Tela (St. Petersburg)* **41** (7), 1297 (1999) [*Phys. Solid State* **41**, 1185 (1999)].

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