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Abstract. The pressure dependences of the heat capacity and T_0 of the bromo-elpasolites Cs$_2$NaYBr$_6$ and Cs$_2$NaTmBr$_6$ were investigated. It is shown that it is possible to describe the experimental results on the grounds of thermodynamic theory.

1. Introduction

The thermodynamic properties of crystals with an elpasolite structure have so far been studied only for chlorides and fluorides (Gorev *et al* 1985, 1986). It was found that the cubic-to-tetragonal phase transitions (PTs) in spite of order are characterized by the same value of entropy change and positive sign of the PT temperature T_0 shift under hydrostatic pressure. Also these characteristics differ from the values for perovskites (Flerov and Gorev 1989). To resolve the question of whether this peculiarity is common to all haloid elpasolites, we studied in the present paper the heat capacity of two bromo-elpasolites Cs$_2$NaYBr$_6$ and Cs$_2$NaTmBr$_6$ and the influence of hydrostatic pressure on the PTs in these compounds. The PT O$_h^5 \rightarrow$ C$_{4h}^5$ in bromides found recently is caused, as in chlorides, by the soft rotatory phonons (Bührer and Güdel 1987).

2. Experimental details

The heat capacity measurements were performed in a vacuum adiabatic calorimeter using single-crystal samples of the following masses: 2.64 g for Cs$_2$NaYBr$_6$ and 3.63 g for Cs$_2$NaTmBr$_6$. Both intermittent- and continuous-heating (and cooling) regimes were used. In the first case the temperature step was 0.3 K in the temperature range near the heat capacity anomaly. The second method is thermographic with a rate $|dT/dt|$ of temperature change of about 5.5×10^{-5} K s^{-1}. This allowed us to investigate the vicinity of T_0 to resolve the question of the order of the PTs.

The pressure dependence of T_0 was measured by the DTA method.

Experimental details concerning Cs$_2$NaYBr$_6$ have been published (Gorev *et al* 1989), and therefore in this paper we shall demonstrate graphs only for Cs$_2$NaTmBr$_6$.
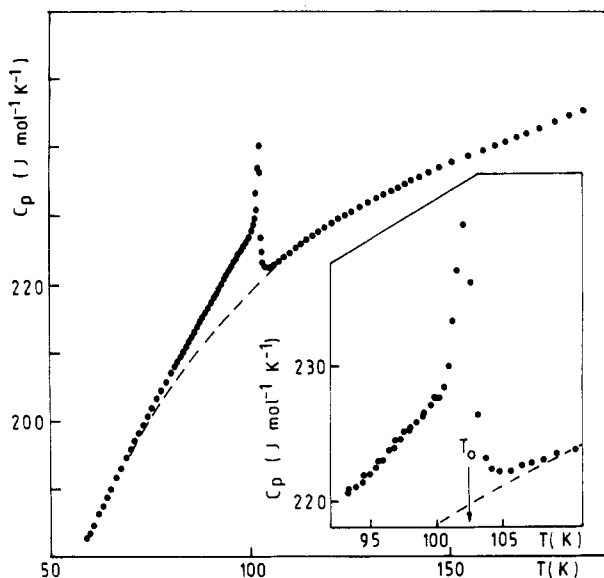
Figure 1. The heat capacity of $Cs_2NaTmBr_6$. The inset is an enlarged view around T_0: - - - lattice contribution.

3. Results and discussion

The heat capacities of the two bromo-elpasolites investigated behave quite similarly. In figure 1, one can see the dependence of C_p on temperature for $Cs_2NaTmBr_6$ from 60 to 185 K. An enlarged view around T_0 is shown in the inset. The lattice and anomaly contributions, ΔC_p, to the heat capacity were separated by graphic extrapolation of $C_p(T)$ for the cubic phase at low temperatures. The excess heat capacity occurs over a wide region below T_0 but only in a small interval $(T_0 + 5 \text{ K})$ for the cubic phase of both crystals. Both the enthalpy and the entropy changes connected with PTs were determined by integration of the areas under the $\Delta C_p(T)$ and $(\Delta C_p/T)(T)$ curves:

$$Cs_2NaYBr_6: \Delta H = 250 \text{ J mol}^{-1} \qquad \Delta S = 1.91 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$Cs_2NaTmBr_6: \Delta H = 172 \text{ J mol}^{-1} \qquad \Delta S = 1.75 \text{ J mol}^{-1} \text{ K}^{-1}.$$

These ΔH-values are much higher than those obtained for the bromo-elpasolites with atoms of Ho (37.3 J mol^{-1}) and Dy (55.8 J mol^{-1}) (Bührer and Güdel 1987). The large difference in ΔH is caused most probably by the impossibility of detecting, by the DSC method, the small excess heat capacity which occurs for elpasolites over a wide temperature interval of the tetragonal phase (figure 1). In fact the comparison of ΔH for $Cs_2NaHoBr_6$ and $Cs_2NaDyBr_6$ with the latent heat δH for Cs_2NaYBr_6 (table 1) and some chlorides (Flerov *et al* 1983, Gorev *et al* 1986) confirms this. The increase in ΔH with increasing T_0 found for chlorides perhaps also occurs for bromides. The total entropy changes $\Delta S/R$ for both crystals investigated in this paper are the same as for chloro- and fluoro-elpasolites (table 1) (Gorev *et al* 1985).

The PT temperatures T_0 were determined by the thermographic method and both an enthalpy jump δH and the hysteresis behaviour of the phase change δT_0 were detected

Table 1. The thermodynamic parameters of the PTs for some elpasolites. τ_{min} to τ_{max} is the temperature interval where the value $(\Delta C_p/T)^{-2}$ behaves according to (1); $\tau = (T_0 - T)/T_0$.

	Cs$_2$NaTmBr$_6$	Cs$_2$NaYBr$_6$	Cs$_2$NaPrCl$_6$[a]
T_0 (K)	102.4 ± 0.2	139.1 ± 0.2	152.6 ± 0.2
δT_0 (K)	0.57	0.18	0.20
δH (J mol^{-1})	5.7	31	47
$\Delta S/R$	0.21	0.23	0.21
dT_0/dp (K kbar^{-1})		4.5	4.8
$(\tau_{min}$ to $\tau_{max}) \times 10^2$	1 to 12	0.4 to 6.0	0.7 to 5.6
$T_0 - T_c$ (K)	14.0	3.6	2.8
A_T (10^{25} J K^{-1} m^{-5})	2.67	1.40	1.80
B' (10^{47} J m^{-7})	−12.9	−2.8	−4.0
C (10^{68} J m^{-9})	11.1	4.0	8.0
N	−0.43	−0.19	−0.16

[a] Gorev *et al* (1986)

(table 1). These results show that the PTs $O_h^5 \rightarrow C_{4h}^5$ in bromo-elpasolites are first order as in chloro-elpasolites. Using the same sample of Cs$_2$NaTmBr$_6$ neutron scattering experiments were carried out earlier and $T_0 = 101.1 \pm 0.5$ K (Bührer and Güdel 1987) was obtained, a value a little lower than that found in this paper. This may be explained from our viewpoint by the different methods of T_0 determination.

The shift of T_0 under hydrostatic pressure was measured unfortunately only for Cs$_2$NaYBr$_6$ (table 1). Because of the smallness of the latent heat (table 1) it was impossible to detect a PT in Cs$_2$NaTmBr$_6$ by the DTA method. The sign of dT_0/dp is positive as in chlorides and fluorides. The strength of the coupling between the order parameter and acoustic degrees of freedom is characterized by the value $\zeta = T_0^{-1}$ dT_0/dp. The order parameter in elpasolites is the displacement of halogen atoms due to octahedra tilts (Aleksandrov and Misyul 1981). There is a good agreement between the ζ-values for Cs$_2$NaTmBr$_6$ (3.25×10^{-2} kbar^{-1}) and for chlorides (3.1×10^{-2} kbar^{-1}) (Flerov and Gorev 1989). In the case of strong coupling (large ζ value) the PTs are usually first order and there are no critical fluctuations near T_0 (Bruce and Cowley 1981).

Earlier it was shown that the thermodynamic properties of fluoro- and chloro-elpasolites which were characterized by a large ζ could be explained on the grounds of the Landau theory (Flerov and Gorev 1989). According to the thermodynamic potential given by Aleksandrov and Misyul (1981) the excess heat capacity for the first-order PT is described by the following expression (Aleksandrov and Flerov 1979):

$$(\Delta C/T)^{-2} = (B')^2/A_T^4 + (12C/A_T^3)(T_0 - T) \tag{1}$$

where A_T, B' and C are coefficients of the thermodynamic potential.

The dependences of $(\Delta C_p/T)^{-2}$ on temperature for both bromo-elpasolites investigated by us are linear functions over rather a wide temperature range below T_0. In figure 2, data for Cs$_2$NaTmBr$_6$ are shown. In the vicinity of T_0 there are deviations from linearity for Cs$_2$NaTmBr$_6$ ($T_0 - T \leqslant 1.5$ K) and for Cs$_2$NaYBr$_6$ ($T_0 - T \leqslant 0.5$ K). Most probably these arise because the sample defects smear out the enthalpy jump; this was observed during thermographic experiments on both crystals. From the linear
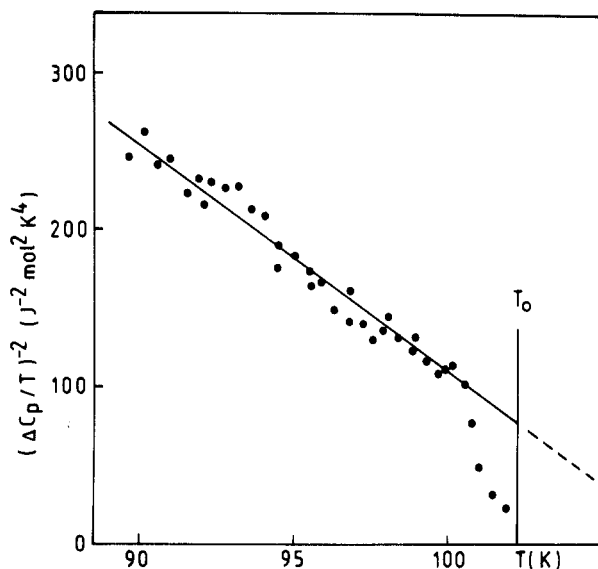
Figure 2. Temperature dependence of $(\Delta C_p/T)^{-2}$: ——, predicted by (1).

temperature dependences of $(\Delta C_p/T)^{-2}$ the relations between the thermodynamic potential coefficients were determined (table 1).

The PT in $Cs_2NaTmBr_6$ is connected with the softening of rotatory mode at the Γ point (Bührer and Güdel 1987) as in chloro-elpasolites (Knudsen 1984, Prokert and Aleksandrov 1984). Over the wide temperature region of the cubic phase, its frequency squared is linear. This means that a Landau-like behaviour is observed. Thus it allows us to determine the coefficient A_T from the following expression:

$$\hbar^2\omega^2 = (2\hbar^2 A_T/M)(T - T_c) \tag{2}$$

where M is the mass density of bromine atoms taking part in the critical vibrations: $M = 16m_{Br}/a^3$, where a is the cubic unit-cell parameter. For Cs_2NaYBr_6 the coefficient A_T (table 1) was determined from calorimetric and ESR data (Gorev *et al* 1989). The latter experimental method allowed us to obtain temperature dependence of the tilt angle φ for the YBr_6 octahedron. The value of φ at $T_0 - T \simeq 40$ K is about 6.5°. For comparison the tilt angle for $Cs_2NaHoBr_6$ is about 4° (Bührer and Güdel 1987). Other coefficients of the thermodynamic potential were obtained from (1). In table 1, besides the coefficients, other thermodynamic parameters are also listed. Among these there is a degree of closeness of PT to the tricritical point $N = -[(B')^2/3A_TCT_c]^{1/2}$ (Aleksandrov and Flerov 1979).

Comparison of this value for bromo- and chloro-elpasolites (table 1) (Flerov *et al* 1983) shows that the first-order PT in $Cs_2NaTmBr_6$ is rather far from the tricritical point. It was observed also in thermographic experiments where the T_0 hysteresis for this crystal was found to be three times higher than for other elpasolites. The difference $T_0 - T_c \simeq 14$ K and so is rather large. It is necessary to point out that the ionic radii of Tm and Y (Shannon 1976) and the cubic unit-cell parameters of $Cs_2NaTmBr_6$ (Bührer and Güdel 1987) and of Cs_2NaYBr_6 (Usachev *et al* 1989) are almost equal to each other. It would be interesting to investigate the heat capacity of other bromides with the rare-earth elements (Ho and Dy) to determine the thermodynamic characteristics.

4. Conclusions

Thus the investigations of the thermodynamic properties of $Cs_2NaTmBr_6$ and Cs_2NaYBr_6 showed that the entropy change and both the sign and the value of ζ are universal characteristics of PTs in haloid elpasolites.

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