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Pressure and temperature electron paramagnetic resonance studies of $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$ crystal

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Abstract. The effect of temperature and hydrostatic pressure on the spin-Hamiltonian parameter b_4^0 for Gd^{3+} in elpasolite $\text{Cs}_2\text{NaLaCl}_6$ is studied up to a pressure of 700 MPa over the temperature range 180–360 K. It is found that 56% of the temperature change in $b_4^0(T)$ is caused by the spin–phonon interaction, and the remaining 44% is related to the thermal expansion of the crystal. The temperature at which the phase transition from the cubic to the tetragonal phase occurs ($T_c = 207$ K) is a linear function of pressure, with the pressure coefficient $dT_c/dp = 53 \pm 0.6$ K GPa^{-1} . The dependence of T_c on the lattice constant and hydrostatic pressure is interpreted within the rigid-sphere model. No precursive behaviour above T_c is observed.

1. Introduction

Comprehensive EPR studies of the temperature and pressure dependencies of the parameter b_4^0 were performed for halide perovskite crystals doped with Gd^{3+} ions (Rewaj *et al* 1992, Krupski *et al* 1996). It was found that the temperature dependence of b_4^0 is predominantly caused by spin–phonon interactions (65%–69% of the total temperature dependence). The effects of pressure on the critical phenomena in the vicinity of the phase transition were observed by the EPR method for $\text{RbCaF}_3:\text{Gd}^{3+}-\text{O}^{2-}$ (Krupski and Buzaré 1994) crystals.

It is of interest to perform similar investigations for other complex cubic crystals. We have chosen a crystal with the elpasolite structure, $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$, which belongs to the chloride family of crystals $\text{Cs}_2\text{NaB}^{3+}\text{Cl}_6$ ($\text{B}^{3+} = \text{Bi}, \text{Nd}, \text{Pr}, \text{La}$). These crystals, widely studied by various methods (Frelov *et al* 1994), exhibit a phase transition from the cubic O_h^5 to the tetragonal C_{4h}^5 phase.

We shall describe the pressure and temperature EPR studies of the spin-Hamiltonian parameter b_4^0 for $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$ ($T_c = 207$ K) in the cubic phase as well as in the phase transition region. The dependence of the phase transition temperature T_c on the hydrostatic pressure, dT_c/dp , is interpreted using the rigid-sphere model (Krupski 1983, 1989).

2. Experiment

Single crystals of $\text{Cs}_2\text{NaLaCl}_6$ doped with Gd^{3+} were grown by the Bridgman method in evacuated and sealed quartz ampoules at the Zavoisky Physical–Technical Institute, Kazan. The Gd^{3+} ion enters the La^{3+} octahedral site.

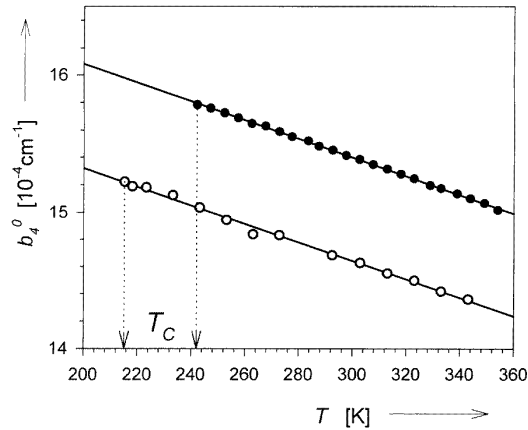


Figure 1. The temperature dependence of the spin-Hamiltonian parameter b_4^0 for $\text{Cs}_2\text{NaLaCl}_6$ single crystal doped with Gd^{3+} at 100 MPa (open circles) and at 600 MPa (full circles).

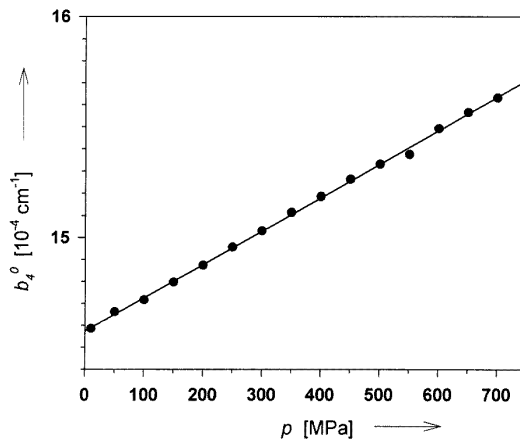


Figure 2. The hydrostatic pressure dependence of the spin-Hamiltonian parameter b_4^0 for $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$ at room temperature.

EPR measurements under high hydrostatic pressure were performed at the Institute of Molecular Physics (Poznań), applying a specially designed spectrometer (Krupski 1996) which is a modified version of an apparatus described previously (Stankowski *et al* 1976). At present, it can be used up to 800 MPa over the temperature range 80–400 K. Pressure and temperature are regulated simultaneously with the high accuracy required for the study of EPR in the vicinity of the phase transition in solids.

The sample of $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$, cut along [001] axis into a cylinder 5 mm long and 2 mm in diameter, was placed in the centre of the corundum resonator, whose cylindrical axis was perpendicular to the direction of the static magnetic field.

3. Results

The temperature dependences of the absolute value of the spin-Hamiltonian parameter b_4^0 for $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$ in the cubic phase are shown in figure 1 for pressures of 100 MPa

and 600 MPa. Both graphs for $b_4^0(T)$ in the temperature range from T_c up to 350 K are linear, with the slope

$$(\partial b_4^0/\partial T)_p = -(68.0 \pm 0.5) \times 10^{-8} \text{ cm}^{-1} \text{ K}^{-1}.$$

No deviation from the linear dependence near T_c was observed.

The measurement of the b_4^0 -variations under the influence of hydrostatic pressure up to 700 MPa was carried out at room temperature. A linear dependence has been obtained (figure 2), with the slope

$$(\partial b_4^0/\partial p)_T = (15.5 \pm 0.5) \times 10^{-8} \text{ cm}^{-1} \text{ MPa}^{-1}.$$

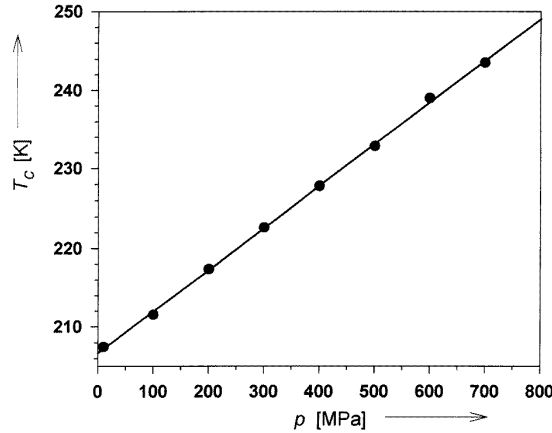


Figure 3. The phase diagram of $\text{Cs}_2\text{NaLaCl}_6$ determined by means of EPR.

The influence of hydrostatic pressure on the phase transition was studied in detail up to 700 MPa. T_c is defined as the temperature at which the cubic spectrum vanishes. $T_c(p)$ is a linear function of the pressure, with the pressure coefficient $dT_c/dp = 53 \pm 0.6 \text{ K GPa}^{-1}$ (figure 3), and this value is the same as the one obtained by the method of differential thermal analysis (Frelov *et al* 1994).

4. Discussion

4.1. The separation volume and phonon effects

The temperature dependence contains thermal expansion and spin-phonon contributions which may be separated using the following thermodynamic relation:

$$\left(\frac{\partial b_4^0}{\partial T}\right)_v = \left(\frac{\partial b_4^0}{\partial T}\right)_p - \frac{\beta}{\kappa} \left(\frac{\partial b_4^0}{\partial p}\right)_T \quad (1)$$

where β is the volume thermal expansion coefficient, and κ is the volume compressibility coefficient.

The value of κ is not known for $\text{Cs}_2\text{NaLaCl}_6$. The elastic stiffness values are only known for $\text{Cs}_2\text{NaBiCl}_6$ (Prokert and Aleksandrov 1984), and from these κ may be calculated. Since the κ -values for all of the compounds of the $\text{Cs}_2\text{NaMCl}_6$ ($M = \text{Bi}, \text{Nd}, \text{La}, \text{Pr}, \text{Sm}, \text{Ce}$) family should nearly the same, then for $\text{Cs}_2\text{NaLaCl}_6$ we assume that $\kappa = (48 \pm 2) \times 10^{-3} \text{ GPa}^{-1}$.

β is determined from the temperature dependence of the lattice constant of $\text{Cs}_2\text{NaLaCl}_6$ in the cubic phase (see figure 1 in Frelov *et al* 1994): $\beta = (9.3 \pm 0.5) \times 10^{-5} \text{ K}^{-1}$. From these values of κ and β , and according to relation (1), the contribution to $b_4^0(T)$ resulting from lattice vibrations is estimated to be

$$(\partial b_4^0/\partial T)_V = -38 \times 10^{-8} \text{ cm}^{-1} \text{ K}^{-1}.$$

This represents 56% of the total temperature changes in b_4^0 , and 44% can be related to the thermal expansion of the crystal, as for Gd^{3+} ions in the fluoroperovskite crystals (Rewaj *et al* 1992), as well as for $\text{CsCaCl}_3:\text{Gd}^{3+}$ (Krupski *et al* 1996).

The empirical dependence of the b_4^0 -parameter upon the metal–ligand distance r is of the form

$$b_4^0 \propto r^k.$$

Hence, by differentiation, the exponent may be determined from the expression

$$k = -\frac{3}{b_4^0 \kappa} \left(\frac{\partial b_4^0}{\partial p} \right)_T. \quad (2)$$

From the experimental data we obtain $k = -6.6$ for $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$.

This value of k is about three to four times smaller than for fluoroperovskite crystals (Rewaj *et al* 1992), and is comparable with the value of k for the simple fluorides $\text{MF}_2:\text{Gd}^{3+}$ (Rewaj *et al* 1992) and for $\text{CsCaCl}_3:\text{Gd}^{3+}$ (Krupski *et al* 1996). It depends on the magnitude of the parameters in equation (2). For Gd^{3+} in CsCaCl_3 and $\text{Cs}_2\text{NaLaCl}_6$, the ratio $(\partial b_4^0/\partial p)_T/\kappa$ amounts to 0.32, and is approximately equal to the appropriate ratio for the fluoroperovskites (see table 1 in Rewaj *et al* 1992). So, the difference between the value of k for the fluoroperovskites and that for the above-mentioned chlorides is mainly caused by the value of b_4^0 being three to four times smaller for fluoroperovskites.

The deviation of the curve for $b_4^0(T)$ from a linear dependence near T_c for the perovskite crystals (Krupski and Buzaré 1994, Krupski *et al* 1996) is not observed for the $\text{Cs}_2\text{NaLaCl}_6:\text{Gd}^{3+}$ system. This precursive behaviour of b_4^0 for the perovskites is explained by the local rotational fluctuations in the cubic phase, which increase under pressure. The EPR of gadolinium-doped elpasolite crystal does not exhibit such a precursive behaviour. This suggests that either the rotational fluctuations are absent, or their frequency is too high in comparison to the EPR frequency.

4.2. The rigid-sphere-model interpretation

The dependence of T_c as a function of the lattice constant for elpasolite compounds was successfully explained by means of the rigid-sphere model (Krupski 1983, 1989). Now, we apply this model to the calculation of the pressure derivatives, dT_c/dp , for the chloride elpasolite family of $\text{Cs}_2\text{NaMCl}_6$ compounds with $\text{M} = \text{Bi}, \text{Sm}, \text{Nd}, \text{Pr}, \text{Ce},$ and La . It was established that the increase of the unit-cell parameter leads to an increase of the phase transition temperature. In figure 4, the experimental values of T_c for these compounds are plotted as a function of the lattice constants extrapolated down to T_c . A solid straight line represents the linear regression of the data. The value of the lattice constant a_0 corresponding to the origin of the line at $T_c = 0 \text{ K}$ is used to calculate of the effective radii of the Cs^+ ion ($R_c = 0.179 \text{ nm}$) and the I^- ion ($R_X = 0.196 \text{ nm}$) in the manner described by Krupski (1989). In particular

$$T_c = \frac{4\pi}{3k} R_h^2 (R_h - R_c) (p + p_l)$$

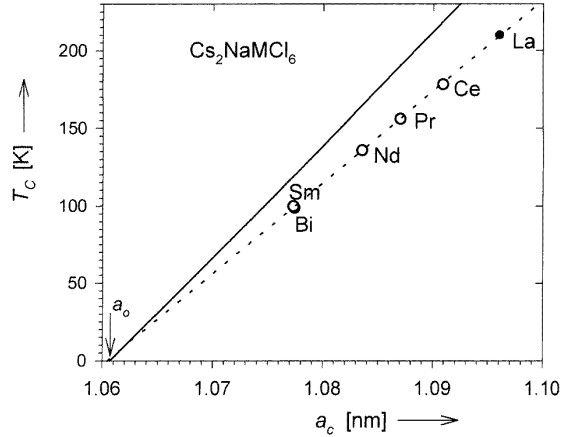


Figure 4. The phase transition temperature versus the lattice constant at T_c for elpasolite $\text{Cs}_2\text{NaLaCl}_6$ compounds with $M = \text{Bi}, \text{Sm}, \text{Nd}, \text{Pr}, \text{Ce},$ and La (dotted line: the linear regression of the experimental data; solid line: the rigid-sphere model).

with the effective radius of the cavity $R_h = a\sqrt{2}/4 - R_X$, and with the lattice pressure p_l (the electrostatic and dispersion contributions) calculated according to equations (19)–(21) published previously (Krupski 1989) for the rigid MCl_6 octahedron ($k = 0$). The effective ionic charges $q_A = +0.38$, $q_B = +0.34$, and $q_X = -0.35$, determined from the phonon dispersion curves for the cubic phase, are known for $\text{Cs}_2\text{NaTmBr}_6$ (Bührer and Güdel 1987). Following Krupski (1989), we use these values in our calculations of the electrostatic contribution to the lattice pressure.

In order to calculate the magnitude of dT_c/dp , we assume first that hydrostatic pressure affects the lattice constant according to

$$a_p = a(1 - \beta p)$$

and secondly that the external pressure modifies the ionic radii proportionally to the magnitude of the pressure:

$$R_{Xp} = R_X(1 - \gamma_X p) \quad R_{cp} = R_c(1 - \gamma_c p)$$

where β is the linear compressibility of the crystal, and γ_X and γ_c are the compressibilities of the corresponding ions.

Because of the thermal vibrations and the free space between the ions, γ_X and γ_c should be less than β . Since it is difficult to estimate the ionic compressibility, we assume that

$$\gamma_X = \gamma_c = 0.75\beta = \frac{0.75}{3}\kappa = 0.012 \text{ GPa}^{-1}$$

which is a reasonable value for the ionic crystals.

Taking into account the above modifications of the rigid-sphere model, we calculate the phase transition temperature at atmospheric pressure T_c versus the lattice constant (figure 4—the solid line), as well as the pressure derivative of T_c , dT_c/dp , as a function of T_c (figure 5—the solid line). The average slope of the theoretical line in figure 4 is 7280 K nm^{-1} , which is more than the experimental value of $5880 \pm 60 \text{ K nm}^{-1}$ (the dotted line). The simplicity of the model may be the main source of these discrepancies—in particular, the effective ionic charges are based on data for bromide elpasolite $\text{Cs}_2\text{NaTmBr}_6$ (Bührer and Güdel 1987), and the data of the dispersion energy are quoted from results for cubic antiferroite

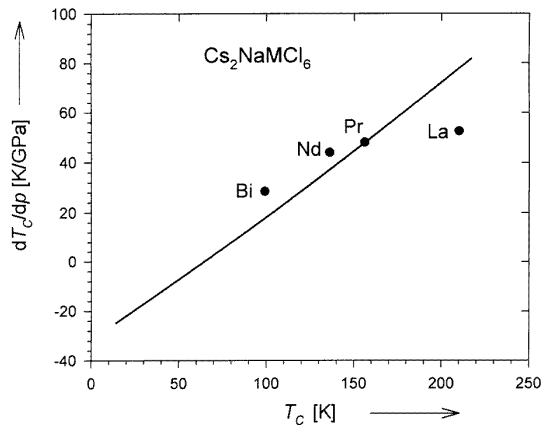


Figure 5. The variation of dT_c/dp with T_c for $\text{Cs}_2\text{NaLaCl}_6$ (experimental data for $M = \text{Bi}$, Nd , Pr , and La ; solid line: the rigid-sphere model).

K_2PtCl_6 (Jenkins 1977). Until now there have been no data available on the ionic charges and the dispersion constants for the family of $\text{Cs}_2\text{NaMCl}_6$ compounds. Moreover, in our calculations the repulsion overlap forces between the central cation Cs^+ and the surrounding Cl^- ions have not been taken into account.

The experimental dependence dT_c/dp on T_c for the family of $\text{Cs}_2\text{NaMCl}_6$ compounds (figure 5) is not linear, and tends to saturation, whereas from the rigid-sphere model a nearly linear dependence is anticipated. It maybe that this discrepancy could be explained by the interaction between the ion Na^+ and the octahedrally positioned surrounding Cl^- ions. But this interaction is difficult to evaluate, due to the lack of appropriate experimental data. Thus, a consistent model describing the phase transitions in elpasolites remains to be obtained.

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