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Single crystal EPR study of trivalent gadolinium in $\mathrm{Cs_2NaInCl_6}$ in the 6 – 300 K interval

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A cubic symmetry site is reported for $\mathrm{Gd^{3+}}$ in $\mathrm{Cs_2NaInCl_6}$ at room temperature. The temperature dependence of the cubic spin-Hamiltonian parameter has been measured in the temperature interval 6–300 K using electron paramagnetic resonance (EPR) spectrometry. A thorough EPR examination for a crystal sample clearly demonstrates that there are no new symmetry sites arising in the temperature interval under study (6-300 K) suggesting, therefore, that the site symmetry remains cubic. We fit an analytical expression for the cubic spin-Hamiltonian parameter b_4^0 as a function of temperature. The absolute sign of this spin Hamiltonian parameter is also determined.

Keywords: Electron paramagnetic resonance (EPR); Elpasolite crystals; S-state ions; $\mathrm{Gd^{3+}}$.

Se reporta un sitio de simetría cúbica para $\mathrm{Gd^{3+}}$ en $\mathrm{Cs_2NaInCl_6}$ a temperatura ambiente. Se mide la dependencia con la temperatura del parámetro cúbico del Hamiltoniano de spin en el intervalo de 6 a 300 K por medio de resonancia paramagnética electrónica (RPE). Un examen detallado del cristal, por RPE, demuestra claramente que no hay sitios con nuevas simetrías en el intervalo de temperatura estudiado, sugiriendo, por lo tanto, que la simetría del sitio permanece cúbica. Adaptamos una expresión analítica en función de la temperatura para el parámetro cúbico del Hamiltoniano de spin. Además se determina el signo absoluto de este parámetro.

Descriptores: Resonancia paramagnética electrónica; elpasolitas; iones estado S; $\mathrm{Gd^{3+}}$.

PACS: 75.10.Dg; 75.30.-v; 76.30.Kg; 32.30.Dx

1. Introduction

This paper is part of a continuing study using electron paramagnetic resonance (EPR) in a wide temperature interval, of S ground state ions used as paramagnetic probes in several crystalline systems in an attempt to provide more experimental information leading to a better understanding of the complex problem of the S-ground state splittings. It has been reported in the past several studies on S-state ions ($\mathrm{Mn^{2+}}$, $\mathrm{Eu^{2+}}$) in alkali halide crystals [1-8]. Recently [9-12] we have carried out studies on elpasolite crystals with the chemical formula $\mathrm{Cs_2NaRCl_6}$ (with R a trivalent ion) in which R = La and Y. In both elpasolites studied the paramagnetic impurity was $\mathrm{Mn^{2+}}$ and $\mathrm{Eu^{2+}}$; cesium-sodium-trivalent ion hexachlorides form part of the elpasolite family. They normally exhibit cubic symmetry at room temperature ($\mathbf{O_h^5}$). The unit cell could be described as constituted by the trivalent ion (indium in this work) located at the center of an octahedron formed by the six nearest neighboring chlorine ions. The cesium positive ions are located as the next nearest neighbors and the positive sodium ions are the third nearest neighbors. This elpasolite type compounds of the general formula $\mathrm{Cs_2NaRCl_6}$ have been widely studied by EPR [13-16], electron nuclear double resonance (ENDOR) [17,18], optical absorption spectroscopy [19-24], X-ray diffraction [25,26], and other techniques [27-30], but very few in the past, yet more in recent years, have been aimed of the study of the field splitting parameters as a function of temperature [31-38]. Several authors [31,32,39] have shown that the change in the splitting at zero field produced by a change in temperature can be expressed as:

$$b_4^0 = \sum_{i=0}^{m} a_i T^i + a_{m+1} \coth \frac{\theta}{2T} \tag{1}$$

in which the first term represents the thermal expansion of the lattice in the vicinity of the paramagnetic ion [40-41] and the second represents the contribution due to lattice vibrations, where T is the absolute temperature, θ is the Debye temperature of the system and a_i the expansion coefficients which are determined from the experiment. However a_0 represents the static contribution at $T = 0$ K and a_{m+1} is proportional to the fundamental phonon frequency also at $T = 0$ K.

In this work we present the results of the temperature variation of the cubic spin Hamiltonian parameters b_4^0 and b_6^0 of $\mathrm{Gd^{3+}}$ in the $\mathrm{Cs_2NaInCl_6}$ elpasolite. A fit of the analytical expression (1) for the predominant parameter b_4^0 as a function of temperature is obtained and discussed.

2. Experimental

Gadolinium doped single crystals of $\mathrm{Cs_2NaInCl_6}$ were grown by mixing the appropriate stoichiometric amounts of CsCl (99.5% purity from Merck) , NaCl (99.98% purity from J.T. Baker) and $\mathrm{In_2O_3}$ (99.999% purity from Aldrich Chemical Co.). The $\mathrm{InCl_3}$ was prepared from $\mathrm{In_2O_3}$ by standard chemical methods. A modification of method A [42,43] described by Morss et al [44] was employed for crystal growth, and optically clear cylindrical shaped crystals 4 mm in diameter and one cm long were obtained by the Bridgman method in evacuated and sealed quartz crucibles. EPR data were obtained using a conventional homodyne spectrometer equipped with a cylindrical cavity (TE$_{011}$ mode) with 100 kHz modulation at different temperatures in the 6-300 K range. Experiments were performed on single crystals. Accurate measurements of the static magnetic field and of the operating microwave frequency were obtained with the aid of an NMR gaussmeter and a frequency counter, respectively. For low temperature measurements, an ITC^{502} (Oxford) variable temperature controller unit was employed.

3. Results

The crystals used in this investigation are related to the elpasolite family which at room temperature present the space group symmetry $\mathbf{O_h^5}$. The paramagnetic impurity added (Gd^{3+}) has a 4f^7 electronic configuration and therefore an ^{8}S$_{7/2}$ ground state. The EPR spectrum is formed by seven fine transitions (ΔM$_s$ $= \pm 1$) in a cubic crystal field. The spin-Hamiltonian used to interpret the spectrum is

$$\mathcal{H} = g\mu_B \mathbf{H}\cdot\mathbf{S} + B_4^0\left[\mathbf{O}_4^0 + 5\mathbf{O}_4^4\right] + B_6^0\left[\mathbf{O}_6^0 - 21\mathbf{O}_6^4\right] + \mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S} \quad (2)$$

where g represents the spectroscopic splitting factor, μ_β is Bohr's magneton, **H** is the applied magnetic field, **S** is the electron spin vector operator, **I** is the nuclear spin vector operator, and **A** is the hyperfine interaction tensor. In general, g and **A** are tensor quantities, but they are assumed to be isotropic scalars for the case of an S-state. The second and third terms represent the cubic crystal field, with $B_4^0 (= a/120 = b_4^0/60)$ and $B_6^0 (= b_6^0/60)$ describing the strength of the fourth- and sixth-order cubic crystalline field, where $\mathbf{O}_4^0$, $\mathbf{O}_4^4$, $\mathbf{O}_6^0$ and $\mathbf{O}_6^4$ are the operator equivalent combinations of the angular momentum operators [45]. The last term represents the hyperfine interaction, which for the case of gadolinium is small, and could be neglected. In expressing the crystal-field interaction in the form of Eq. (2), the z direction was found to be along a fourfold cubic axis. Fig. 1a shows the observed spectrum for H$\|$[100] at 300 K. It consists of 7 fine structure lines, which is consistent with the electronic spin of trivalent gadolinium (7/2) in an octahedral coordination. Experimental results show that the lattice of cesium sodium indium hexachloride with gadolinium as a paramagnetic impurity preserves the cubic symmetry over the whole temperature range studied (6–300 K), as can be seen in Fig. 1b where the seven line spectra is still observed at 6.3 K. This is supported by the fact that no new transitions (other than the seven transitions typical of a cubic symmetry) appear over the entire temperature range measured in this study. Moreover, the steady magnetic field angular variation shown in Fig. 2 extended over a $\{011\}$ crystallographic plane of the Cs$_2$NaInCl$_6$:Gd^3+ single crystal, naturally agrees with the cubic nature of the crystallographic system. These spectra

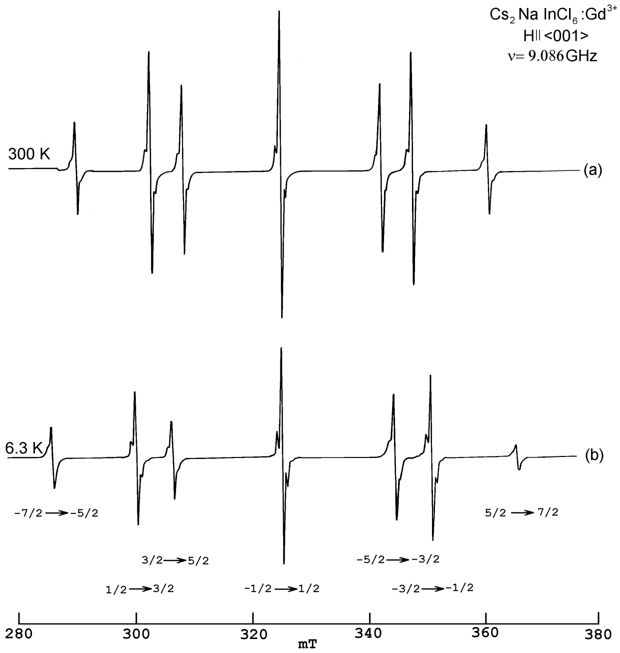

FIGURE 1. Temperature dependence of the Electron Paramagnetic Resonance spectrum of Gd^{3+} in Cs$_2$NaInCl$_6$ (a) 300 K and (b) 6.3 K.

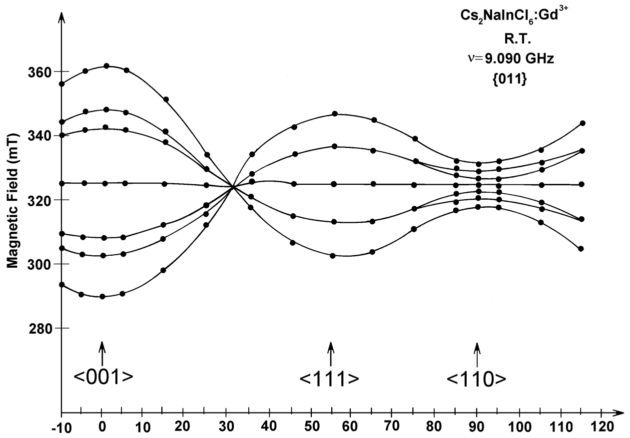

FIGURE 2. Angular variation of the seven fine structure transitions (M$_S$ →M$_{S-1}$) of in Gd^{3+} the $\{011\}$ crystallographic plane at room temperature.

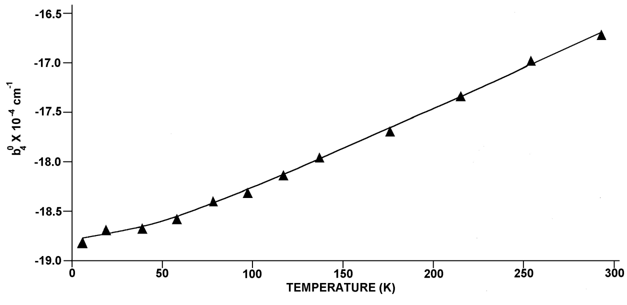

FIGURE 3. b_4^0 parameter as a function of temperature for the Cs$_2$NaInCl$_6$:Gd^{3+} system.

TABLE I. Spin-Hamiltonian parameters,g, b_0^4, b_0^6 as a function of temperature (T) for Gd^{3+} in Cs$_2$NaInCl$_6$. The number in parenthesis are the errors in the last significant digit.

T(K)	g	$b_4^0(10^{-4}\text{cm}^{-1})$	$b_6^0(10^{-4}\text{cm}^{-1})$
6.3	1.9941(3)	-18.8(1)	0.8(2)
20	1.9938(4)	-18.6(1)	0.7(2)
40	1.9940(4)	-18.6(1)	0.8(2)
60	1.9940(4)	-18.5(1)	0.7(2)
80	1.9942(3)	-18.3(1)	0.7(2)
100	1.9942(3)	-18.2(1)	0.7(2)
120	1.9942(4)	-18.1(1)	0.7(2)
140	1.9945(4)	-17.9(1)	0.7(2)
180	1.9943(3)	-17.6(1)	0.6(2)
220	1.9942(4)	-17.2(1)	0.6(2)
260	1.9943(3)	-16.8(1)	0.7(2)
300	1.9943(3)	-16.6(1)	0.6(2)

(6-300 K) could be fitted with cubic spin-Hamiltonian parameters. As expected for a cubic symmetry system, b_4^0 is the predominant parameter and in this particular case, b_6^0 does not appreciably change over the temperature range studied. The results in Table I show the spin Hamiltonian parameters as a function of the temperature. Fig. 3 exhibits the variation of b_4^0 with temperature. The best adjusted curve consistent with Eq. (1) that fits the experimental results reported in Table I has the form

$$b_4^0 = a_0 + a_1 T + a_2 \coth \frac{\theta}{2T} \tag{3}$$

where the Debye temperature θ corresponds to the one that gives the least mean square deviation for the fit. The adjustable parameters a_0, a_1 and a_2 in Eq. (3) were obtained through the least square fit, using the Gauss-Jordan procedure [46]. The results are (with $\theta = 150K$) $a_0 = -19.1845 \times 10^{-4}\text{cm}^{-1}$, $a_1 = 0.0027 \times 10^{-4}\text{cm}^{-1}K{-}1$, $a_2 = 0.4497 \times 10^{-4}\text{cm}^{-1}$ where the mean square deviation between the calculated and reported values is $\sigma = 0.0014 \times 10^{-4}\text{cm}^{-1}$.

4. Conclusions

It is important to note that there is no evidence in the EPR spectra of new peaks developed belonging to another symmetry site in the 6-300 K temperature range. Similar results were already reported [15] for the case of Cs$_2$NaYCl$_6$:Gd^{3+} elpasolite. The best analytical adjustment was obtained with the same cubic spin-Hamiltonian Eq. (2) in the temperature range under study. To check the validity of Eq. (3) of the proposed behaviour of b_4^0 with temperature on the low temperature region, we calculated the value of the predominant cubic parameter at 4 K which turns out to be $-18.8 \times 10^{-4}\text{cm}^{-1}$ to compare it with the value reported by S.M. Akhmin *et al.* [47] as 2.01 mT ($= -18.7 \times 10^{-4}\text{cm}^{-1}$), rendering a difference of less than 0.01%. From Fig. 1b we can determine the absolute sign, for the first time in this system, of the b_4^0 parameter by comparing the intensities of the outermost transitions labeled $-(7/2) \rightarrow -(5/2)$ and $(5/2) \rightarrow (7/2)$ .Their relative intensities show that the absolute sign of b_4^0 is negative.

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