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1994 J. Phys.: Condens. Matter 6 10279

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Thermal-expansion analysis of $\text{KZnF}_3:\text{Mn}^{2+}$ by EPR and absorption spectrum

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Received 20 June 1994, in final form 8 September 1994

Abstract. The thermal expansion of the $\text{Mn}^{2+}-\text{F}^-$ bond for $\text{KZnF}_3:\text{Mn}^{2+}$ in the 15–300 K temperature range has been studied by the electron paramagnetic resonance (EPR) and the absorption spectrum. In this way the linear thermal expansion $\delta R = 16 \times 10^{-4}$ nm and the linear-thermal-expansion coefficient $\alpha = (1/R)(dR/dT) = 27.1 \times 10^{-6} \text{ K}^{-1}$ for $\text{Mn}^{2+}-\text{F}^-$ are obtained at room temperature. The results are in good agreement with the values observed experimentally, indicating a successful interpretation of the crystal-field theory for the thermal expansion.

1. Introduction

$\text{KZnF}_3:\text{Mn}^{2+}$ has received particular attention as its cubic structure provides unusual opportunities for experimental and theoretical investigations. Its electron-paramagnetic-resonance (EPR) spectrum and absorption spectrum have been measured in [1–4]. In cubic symmetry there is only one zero-field splitting parameter a , which is related to the separation between the Γ_8 and Γ_7 energy levels of the ground ${}^6\text{S}$ state by $3a = E(\Gamma_8) - E(\Gamma_7)$ [5]. It can be evaluated by means of diagonalization, as has also been done in [6–10]. Powell *et al* [11] found that the spin–spin coupling contributes a negligible value to a in comparison with the contribution resulting from the spin–orbit coupling. The main aims of the present work are (i) to obtain the energy levels and EPR cubic zero-field splitting parameter a of $\text{KZnF}_3:\text{Mn}^{2+}$ in the 15–300 K temperature range by using the Hamiltonian matrices including the spin–orbit coupling, the crystal field and the Coulomb interaction; (ii) to discover whether the EPR cubic zero-field splitting parameter a is mainly dependent on the spin–orbit and crystal-field interactions within the ground ${}^6\text{S}$ and excited states; (iii) to find whether the effective Racah parameters B and C are independent of R in the range $R = 0.2064\text{--}0.2080$ nm in a very good first approximation while Dq depends significantly on R^{-5} for $\text{KZnF}_3:\text{Mn}^{2+}$; (iv) to reveal the linear thermal expansion $\delta R = 16 \times 10^{-4}$ nm and the thermal-expansion coefficient $\alpha = (1/R)(dR/dT) = 27.1 \times 10^{-6} \text{ K}^{-1}$ for the $\text{Mn}^{2+}-\text{F}^-$ distance at room temperature; (v) to justify the results of the crystal-field theory in the explanation of the cubic zero-field splitting of ${}^6\text{S}$ -state ions in octahedral coordinations and the thermal-expansion effects around an impurity.

2. Theoretical analysis

2.1. Energy levels

Using the irreducible representation basis functions of the double group O_h , we obtain the spin-orbit coupling, the crystal-field and Coulomb interaction matrices of d^5 configuration in the strong-field scheme of Sugano *et al* [12]. The Hamiltonian matrices include Γ_6 , Γ_7 , Γ_8 representations. The matrix elements are expressions of the Racah parameters B and C , the crystal-field parameters Dq , and the spin-orbit coupling coefficient ξ .

In $KZnF_3:Mn^{2+}$, the Mn^{2+} ion is surrounded by six F^- ions, having O_h point-group symmetry. The crystal-field potential of the d^5 configuration with O_h symmetry is expressed as

$$V = \sum_{i=1}^5 -\frac{7\sqrt{\pi}}{3R^5} r_i^4 \left(Z_{40} + \frac{\sqrt{35}}{7} Z_{44}^c \right). \quad (1)$$

Here R is the bonding length, r_i are the coordinates of the d electrons in Mn^{2+} ; Z_{40} and Z_{44}^c denote real spherical harmonic functions.

We employ the parametrization d orbital for Mn^{2+} of Zhao *et al* [13, 14] and obtain the crystal-field parameter Dq

$$Dq = \frac{e^2 \langle r^4 \rangle}{6R^5} \left(1 + \frac{5\mu}{eR} \right) \quad (2)$$

where e denotes the electronic charge, $\langle r^4 \rangle$ the expectation value of r^4 , and μ the electric dipole moment. We employ the correlation formulae for $\mu - \sigma$ [15]:

$$\mu/eR = 0.1666\sigma^{1.1} - 0.0296. \quad (3)$$

Here σ ($=0.64 \times 10^{-24} \text{ cm}^3$) is the electron polarizability of a ligand F^- .

In our calculation, the parametrization d orbital for Mn^{2+} has been used, which gives [13, 14]:

$$B = 911 \text{ cm}^{-1} \quad C = 3273 \text{ cm}^{-1} \quad \xi = 336.6 \text{ cm}^{-1} \quad \langle r^4 \rangle = 23.2594 \text{ au}. \quad (4)$$

The crystal-field parameters can be obtained as long as we know the values of the bond lengths $R_1 = 0.2064 \text{ nm}$ ($T = 15 \text{ K}$) and $R_2 = 0.2080 \text{ nm}$ ($T = 300 \text{ K}$) for $KZnF_3:Mn^{2+}$ [16]. Substitution of these parameters into the Hamiltonian matrices yields the energy levels for $KZnF_3:Mn^{2+}$ ($T = 15 \text{ K}$ and $T = 300 \text{ K}$) separately as given in table 1.

In table 1, the positions of crystal-field excitation peaks corresponding to $KZnF_3:Mn^{2+}$ at temperature $T = 15 \text{ K}$ and at room temperature are reported. It can be seen that the position of the excitation peaks (4A_1 (G), 4E (G) and 4E (D)) which are independent of Dq remains unchanged within experimental errors. This supports the suggestion that we can take the effective Racah parameters B , C and the spin-orbit coupling coefficient ξ as being independent of R within the domain of distances explored.

2.2. EPR cubic zero-field splitting parameter a

One of the most important spin-Hamiltonian parameters of a 6S -state ion is the cubic zero-field splitting parameter a , which is defined by the spin Hamiltonian

$$H_s = (a/6)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{3}S(S+1)(3S^2 + 3S - 1)]. \quad (5)$$

The study of the EPR cubic zero-field splitting parameter a has become very interesting in crystal-field theory as an effective way of investigating the crystalline potentials at the

Table 1. The comparison of theoretical and experimental values (in cm^{-1}). The bands calculated above $35\,000\text{ cm}^{-1}$ have not been listed.

Transition	$\text{KZnF}_3:\text{Mn}^{2+}$ ($T = 15\text{ K}$)			$\text{KZnF}_3:\text{Mn}^{2+}$ ($T = 300\text{ K}$)		
	Experiment [1]	Theory		Experiment [1]	Theory	
${}^6\text{A}_1$ (S) to						
${}^4\text{T}_1$ (G)	18 350	18 340	18 343 18 365	18 530	18 520	18 529 18 555
${}^4\text{T}_2$ (G)	22 590	22 459	22 628 22 721	22 830	22 660	22 837 22 932
${}^4\text{E}$ (G)			25 210			25 210
and	25 210		25 212	25 210		25 212
${}^4\text{A}_1$ (G)			25 214			25 214
${}^4\text{T}_2$ (D)	28 220	27 665	28 295 28 560	28 180	27 706	28 218 28 258
${}^4\text{E}$ (D)	30 080	30 160	30 175	30 080	30 160	30 175
${}^4\text{T}_1$ (P)	32 830	32 429	33 143 33 213	32 750	32 446	33 019 33 098

magnetic ion sites. The parameter a measures the energy difference between the 22×22 matrix of Γ_7 and the 42×42 matrix of Γ_8 representations of ground state ${}^6\text{S}$:

$$3a = E(\Gamma_8) - E(\Gamma_7). \quad (6)$$

Substituting the above parameters into the Hamiltonian matrices, we obtain the EPR cubic zero-field splitting parameter $a_1 = 6.84 \times 10^{-4}\text{ cm}^{-1}$ ($T = 15\text{ K}$, experimental $a_1 = 6.9(1) \times 10^{-4}\text{ cm}^{-1}$, [2]) and $a_2 = 6.21 \times 10^{-4}\text{ cm}^{-1}$ ($T = 300\text{ K}$, experimental $a_2 = 6.3(1) \times 10^{-4}\text{ cm}^{-1}$, [2]) for $\text{KZnF}_3:\text{Mn}^{2+}$. The result is in good agreement with those observed experimentally, which indicates that the spin-spin coupling contributes a negligible value to a in comparison with the contribution resulting from the spin-orbit coupling and omitting the spin doublets reduces the calculated splitting by almost two orders of magnitude.

2.3. Thermal expansion

The properties due to a cation impurity in an ionic lattice mainly depend on the nature and number of nearest anions as well as on the true value of the impurity-ligand distance R . However, the determination of this important parameter and particularly of variations induced by temperature or pressure change is not easy.

In table 1, the crystal-field transitions involving excited states with $S = \frac{3}{2}$ of cubic fluoroperovskites doped with Mn^{2+} are detected. Among these transitions the most sensitive to Dq is the first ${}^6\text{A}_1$ (S)- ${}^4\text{T}_1$ (G) transition. Therefore in the present work we have followed the variations undergone by the ${}^4\text{T}_1$ (G) excitation peak with temperature in order to derive from it the changes experienced in the $\text{Mn}^{2+}-\text{F}^-$ distance. The variation of the absorption spectrum has been followed for several different temperature values.

As a guide in figure 1 of [1], the ${}^4\text{T}_1$ (G) peak energy versus temperature in the range 15–300 K is plotted. It can be seen that below 100 K the energy of this peak lies always at $18\,340\text{--}18\,365\text{ cm}^{-1}$ within experimental error while above this temperature it increases progressively. The constancy of the ${}^4\text{T}_1$ (G) peak energy below 100 K is consistent with the usual weakness of thermal-expansion effects in such a temperature region.

In figure 2 of [1], the value $\delta R(T) = R(T) - R(0)$ derived from the corresponding variations of Dq for the MnF_6^{4-} complex in $\text{KZnF}_3:\text{Mn}^{2+}$ is reported. The value of $\delta R = 16 \times 10^{-4}\text{ nm}$ agrees quite well with the experimental values $\delta R = (12 \pm 1) \times 10^{-4}\text{ nm}$ [1] and $\delta R = (10 \pm 3) \times 10^{-4}\text{ nm}$ previously derived from EPR [17] data for $\text{KZnF}_3:\text{Mn}^{2+}$

at room temperature and therefore it supports the present analysis. In the present case the thermal-expansion coefficient $\alpha = (1/R)(dR/dT) = 27.1 \times 10^{-6} \text{ K}^{-1}$ (the experimental $\alpha = (38 \pm 14) \times 10^{-6} \text{ K}^{-1}$) at room temperature for the $\text{Mn}^{2+}\text{-F}^-$ distance is derived.

3. Results and discussion

The effective Racah parameters B and C are independent of R in a very good first approximation while Dq depends significantly on R , being proportional to R^{-5} .

The theoretical electronic transitions of the MnF_6^{4-} complex can be well obtained by means of the four usual parameters: the effective B and C Racah parameters, the cubic-field splitting Dq and the spin-orbit coupling coefficient ξ . Moreover, there are no free parameters at all and no fitting of parameters to data has been done.

The zero-field splitting parameter a for $\text{KZnF}_3:\text{Mn}^{2+}$ was as the result of spin-orbit and crystal-field interactions within the ground ^6S and excited states.

It can be seen that the method of determining quantitatively the linear thermal expansion $\delta R = 16 \times 10^{-4} \text{ nm}$ and the thermal-expansion coefficient $\alpha = (1/R)(dR/dT) = 27.1 \times 10^{-6} \text{ K}^{-1}$ for the $\text{Mn}^{2+}\text{-F}^-$ distance at room temperature from relevant EPR and optical spectra data is appropriate.

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