Study of Manganese Doped Ammonium Bromide Single Crystal Using EPR Technique

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Abstract: *The energy level splitting and EPR transitions of Mn^{2+} ion have been depicted. Here estimation of ZFS parameter for ammonium bromide single crystal will be carried out quantitatively and compared with those for ammonium chloride. The EPR spectra have been recorded at room temperature as well as liquid nitrogen temperature along with angular variation. The results obtained have been presented and discussed in this paper.*

Keywords: EPR Spectroscopy, metal ions, hyperfine interaction, cubic symmetry

1. Introduction

Divalent manganese has an exactly half filled 3d shell, with ground state $^6S_{5/2}$. Generally, in such cases one does not expect any splitting other than due to the Zeeman interaction. In that case a single line would be observed at the free spin value g=2.0023. Experimentally a complex EPR spectrum is observed displaying both hyperfine and fine structure transitions. Theoretically Bethe suggested that the splitting could arise because of the cubic fields which splits the sextet into a doublet and a quartet. This was found inadequate in accounting the magnitude of the observed splitting. Van Vleck and Penny suggested that the splitting could be accounted by the crystal field and spin orbit interaction. Since then number of research articles have appeared and have explained with some success the ground space splitting. Experimentally Mn^2 ion in diamagnetic host lattices offers an important probe for understanding the host systems structural configuration. The zero field splitting parameter is quite sensitive to the immediate environment around the central ion. The dynamic study of this parameters provides important information about the thermal properties of the system.

It is well known that the properties of pure crystals are modified significantly by intentional creation of lattice point defects in the host lattice. When a diavalent cation substitutes for a monovalent host the charge compensation is required. It is achieved usually by host cation vacancies. Such ion-vacancy (I-V) pairs have been extensively studied in Alkali halides and Ammonium halides using EPR of Transition Metal ion impurities[1-6].

Ammonium halides undergo several phase transitions and in some of them order-disorder of NH_4^+ orientations are believed to play a major role[7-9]. EPR studies on Mn^{2+} doped single crystals of NH_4Cl and NH_4I have shown that there exists a very large crystal field splitting of the $^6S_{5/2}$ configuration and the zero field splitting (ZFS) Parameter D is very large [4-8,10-12] (1600 G) ZFS is extremely large (D~420 mT) for Mn^{2+} ions in CsBr host[13], NH_4Cl is a well studied system as is clear from literature but there exists only one report on EPR study of Mn^{2+} in NH_4Br single crystal with the aim to determine quantitatively the values of ZFS parameter so that the results could be compared with those for NH_4Cl.

2. Theory of EPR of Mn^{2+} ion

The electronic configuration of Mn^{2+} is d^5, with five unpaired electrons the 3d shell is half filled the free ion ground state is $^6S_{5/2}$ and the six fold degeneracy is lifted by way of spin orbit coupling giving rise to three Krammers doublets [14-17]. The spin Hamiltonian describing the EPR spectrum in a cubic crystal field is the following [16-17]

$$H_c = g\beta \vec{B}\cdot\vec{S} + \frac{a}{6}\left(S_x^4 + S_y^4 + S_z^4 - \frac{707}{16}\right) + \vec{I}\cdot\vec{A}\cdot\vec{S} \quad (2.1)$$

Splitting of levels in EPR occurs under the influence of two fields. In crystal fields of symmetry lower than cubic additional ZFS terms in the spin Hamiltonian of equation (2.1) are required to explain the EPR spectra. The spin Hamiltonian appropriate to an Orthorhombic crystal field is of the following form:

$$H = H_c + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E\left[S_x^2 - S_y^2\right]$$
$$+ \frac{F}{18}[35\,S_z^4 - 30S(S+1)\,S_z^2 + 25S_z^2] - 6S(S+1) + 3S^2 (S+1)^2\,] \quad (2.2)$$

where D and E are called axial and rhombic ZFS parameters. For axial symmetry, E = 0 and
$g_z = g_\parallel$; $g_x = g_y = g_\perp$; $A_z = A\perp$; $A_x = A_y = A\perp$

The smaller nuclear zeeman and quadrupole interaction terms are not considered in the above spin Hamiltonian.

3. Experimental Results and Discussion

At room temperature (RT) the EPR spectrum of single crystal of Mn^{2+} doped NH_4Br (to be called AB henceforth) comprised a sextet whose positions were orientation independent (Fig. 1). This is similar to the spectrum-I of ref. (5). On lowering the temperature a new kind of spectrum emerged which became dominant at LNT (Fig. 2). Similar observation was made by Chand and Upreti[6]. This low temperature spectrum was found to be orientation dependent. Taking clues from the observations made by Chand and Upreti we have recorded the spectra in (100) planes which incidentally contain the z-axis of the crystalline field. When the magnetic field is aligned along <100> there are only two sets of sextets (Fig. 2). One is

assigned to $\theta = 0°$ (corresponding to g_{11}) and the other to $\theta = 90°$ (corresponding to $g_\perp$) orientations of magnetic field $\underset{B}{\rightarrow}$,

On changing the orientation of the magnetic field away from

<100> in any direction in the (100) plane the sextet corresponding to $\theta = 0°$ shifts towards lower fields
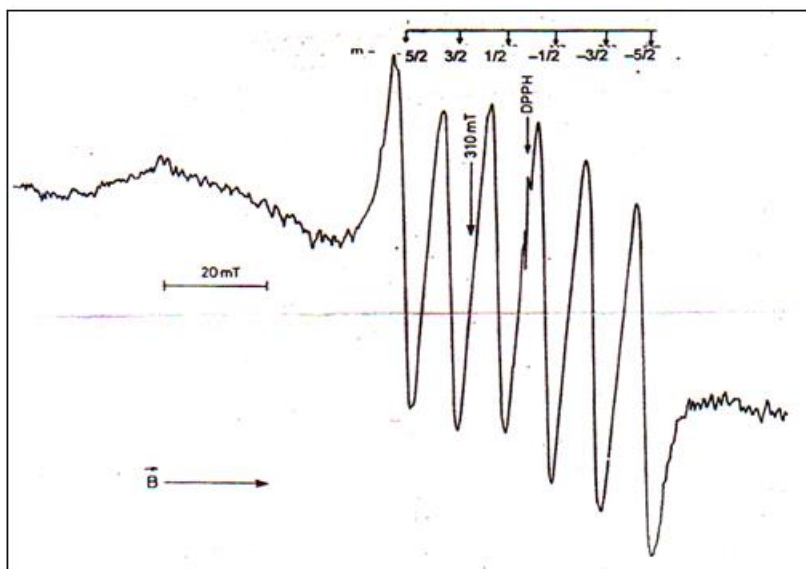

Figure 1: EPR Spectrum of Mn^{2+} doped NH_4Br at room temperature

(sextet marked as C in Fig. 2) whereas sextet corresponding to $\theta = 90°$ splits into two components (sextets marked as a and b in Fig 2) one of which remains stationary and the other moves (sextet marked as b) towards higher fields intervals of 90° rotation in (100) planes the spectra repeats themselves. These observations are in agreement with those reported by Chand and Upreti[6].

The EPR spectrum at LNT, the picture is not normal due to large ZFS-as suggested qualitatively by Chand and Upreti[6]. From the analysis of EPR spectra at LNT we obtained the following parameters.

$$g_\parallel = 2.001 \pm 0.001 \quad g_\perp = 2.002 \pm 0.002$$
$$|A_\perp| = 9.3 \pm 0.2 \, mT ; \quad |A_\parallel| = 9.4 \pm 0.2 \, mT ;$$
$$|D| \sim 330 \, mT$$

Table 1: Large values of ZFS Parameter D for Mn^{2+} ion in some host.

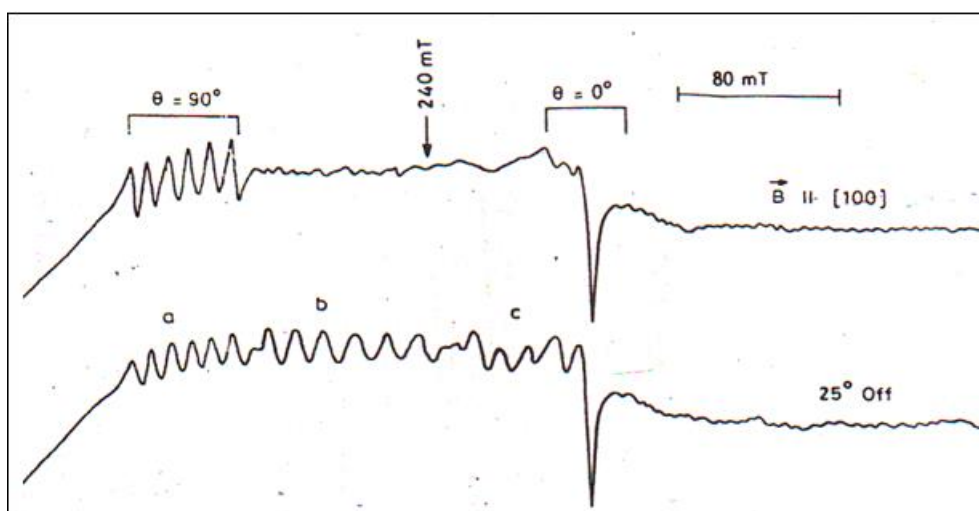| Host	Values of $|D|$
CsCl	137.5 mT ($\sim$ 0.1245 cm^{-1})
CsBr	0.392 cm^{-1}
NH4CL	161.5 mT ($\sim$ 0.1498 cm^{-1})
NH4Br	330 mT ($\sim$ 0.308 cm^{-1})
NH4I	160.2 mT ($\sim$ 0.145 cm^{-1})

Figure 2: EPR Spectra of Mn^{2+} doped NH_4Br at LNT along the two orientations shown against the figures.

4. Conclusions

In the present study we have estimated ZFS parameter quantitatively the Mn^{2+} doped in AB, As expected the value of | D | is very large as compared to normal cases. In Table 1 we have collated large values of | D | which are comparable to the present case and the host compound comprises

halogens. It may be observed from this table that the values of | D | are in the order Cl < Br < I with respect to halogens [20-24]. This sequence is not followed in ammonium halides. However, as expected ZFS is very large for Br compounds as compared to isomorphous Cl compounds of Cs and NH_4. The reversible change between isotropic → anisotropic EPR

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spectra between RT and LNT is attributed to hopping motion of ion-vacancy pairs.

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