EFFECT OF TEMPERATURE AND TIME ON PARAMAGNETIC RESONANCE OF Mn^{2+} IN NaCl SINGLE CRYSTAL

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Abstract

Exchange of intensities among various spectra of Mn^{2+} in NaCl single crystal, corresponding to Mn^{+2} ion associated with various point defects, is described as a function of temperature and time. The variation of line width with temperature is discussed. The fine structure parameter D for a particular spectrum is measured with temperature and is shown to behave like $D = D_0 (1 + bT + cT^2)$. Thermal formation of new complexes and their lifetimes are discussed. A new short-lived complex is found and a model for the same is suggested.

Introduction

Paramagnetic resonance of Mn^{2+} in NaCl single crystal has been recently studied by us[1] in detail. The present paper is in continuation of our earlier two papers to be referred here as Papers I and II. Eight different spectra, designated I, II, III_1, .. VII, are found. Spectrum[2] I consists of a single broad line which comes from the precipitated Mn^{2+} ions. Spectrum[3] II corresponds to Mn^{2+} ions which are isolated from lattice defects and therefore have local cubic symmetry, spectrum[4, 5] III_1 to Mn^{2+} ions associated with a nearest neighbour Na^+ vacancy, and III_2 to those associated with a next nearest neighbour Na^+ vacancy.[6] Spectrum IV (Paper I) corresponds to Mn^{2+}: O_2^{2-} and V (Paper I) corresponds to Mn^{2+} ion associated with an O_2^{2-} molecular ion and a vacancy, VI (Paper I) to Mn^{2+}: OH^- and a probable vacancy and spectrum VII (this Paper) corresponds to Mn^{2+} ion associated with O_2^{2-} molecular ion and probable two vacancies.

The effect of temperature on paramagnetic resonance spectra is, in general, confined to variation in line widths and line intensities. The fine structure

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is known to be effected to some extent by temperature but the hyperfine structure has rarely been found to vary. In cases, where lattice defects are involved in presence of paramagnetic ions, one may expect drastic changes in the spectra, *e.g.*, new spectra may appear due to thermal formation of new complexes. Such complexes may have short lifetimes and the spectra arising due to these will then depend on time. The present paper deals with this type of formation of new complexes and gives an account of variation of fine structure zero field splitting parameter with temperature for spectrum IV of Mn^{2+} in NaCl.

The experimental details are the same as in Paper I. A Varian temperature control unit, V-4540, which works in the range — 180° C.+300° C. has been used for the present studies.

RESULTS AND DISCUSSIONS

As the temperature is lowered spectrum II (*see* Paper I) converts reversibly to spectra III (Figs. 1 and 2). The spectra III are more intense at low temperature while spectrum II is more intense at high temperatures. An intense spectrum II is seen at 250° C. in Fig. 1. The intensities of the spectra III_1 and III_2 are nearly equal showing that they are equally likely in the crystals grown from melts under vacuum. In other crystals, where only the spectra I and IV are present (*see* Paper I) at room temperature it is seen that the spectra II and III appear at high temperature (Fig. 2). This is due to dissolu-

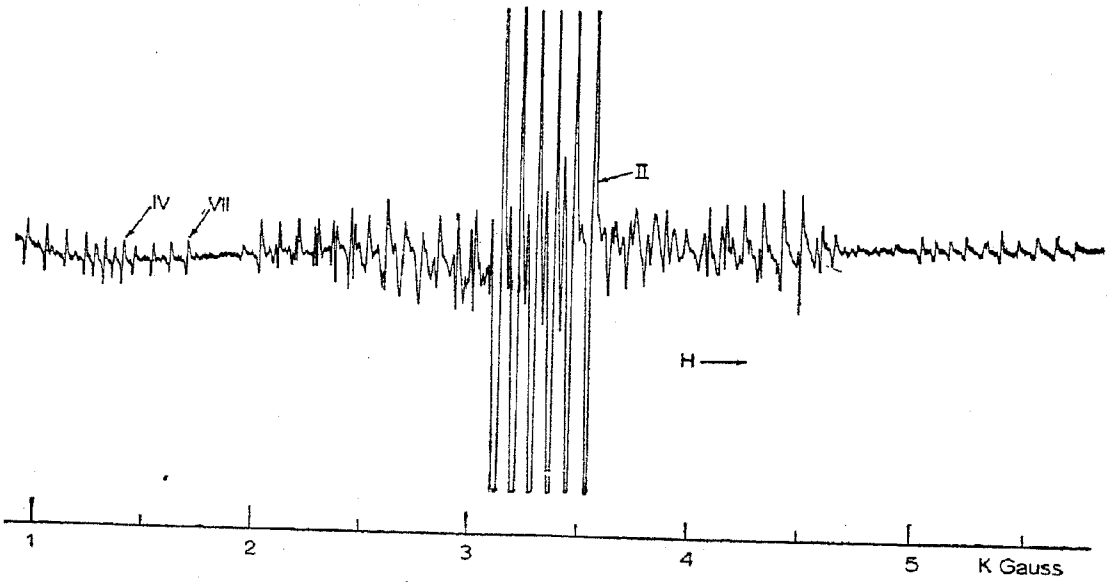

FIG. 1. Spectrum VII in paramagnetic resonance of Mn^{2+} in NaCl at X-band at H// [100] direction at 250° C. An intense spectrum II is seen along with spectrum IV.

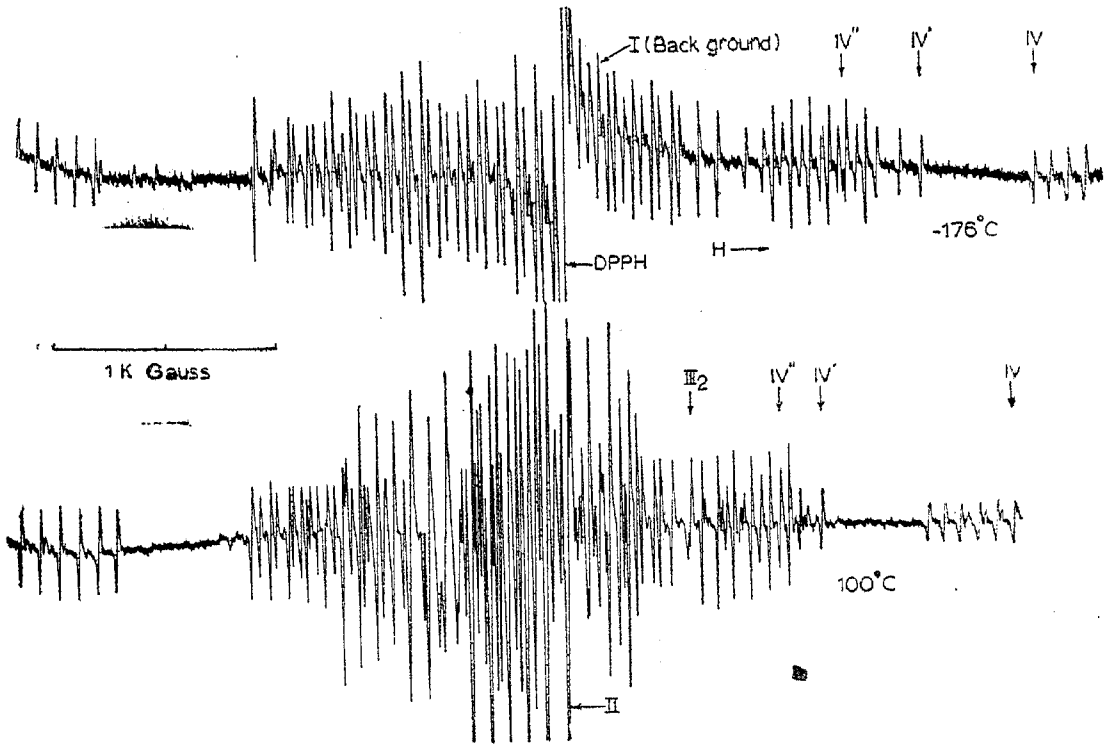

FIG. 2. Paramagnetic resonance spectra of Mn^{2+} in NaCl at $-176°$ C. and at 100° C.; at $-176°$ C., the spectra I and IV are seen. At 100° C. spectra II and III appear along with IV. (IV′ and IV″ are 90° parts of IV) H// [001] direction.

tion of the coagulated Mn^{2+} ions at high temperature. However, when the crystals contained only the spectrum IV at room temperature no other spectrum appeared even up to a temperature as high as 300° C. or as low as $-$ 180° C. showing that the O_2^{2-} molecular ion is very tightly bound to the Mn^{2+} ion in the crystal. The spectrum IV stands with time while the spectra II and III decay with time to the spectrum I.

The line widths of the spectra III are found to increase with increase in temperature which is probably because of the increased hopping of the first and second neighbour alkali vacancies. The line widths of spectrum IV do not change as much with temperature as that of spectra III. This observation confirms that spectrum IV is not associated with any mobile lattice defect.

When the temperature of the crystal is changed in random steps, while in the cavity, short-lived complexes that might be formed due to thermal disturbances will be observed. Thus short-lived vacancy pairs or complexes involving vacancies associated with O_2^{2-} molecular ion or with OH^- ion may be formed. An effect of such phenomena is the appearance of extremely

short-lived spectra. Spectrum VII, marked in Fig. 1, has been observed only for a very short time and is therefore an example of this type. In our Paper I we observed a spectrum V which we assigned to Mn^{2+} ions associated with O_2^{2-} molecular ion and a probable nearby vacancy. This was found to change with time and exchange intensities with spectrum IV (Fig. 3) but

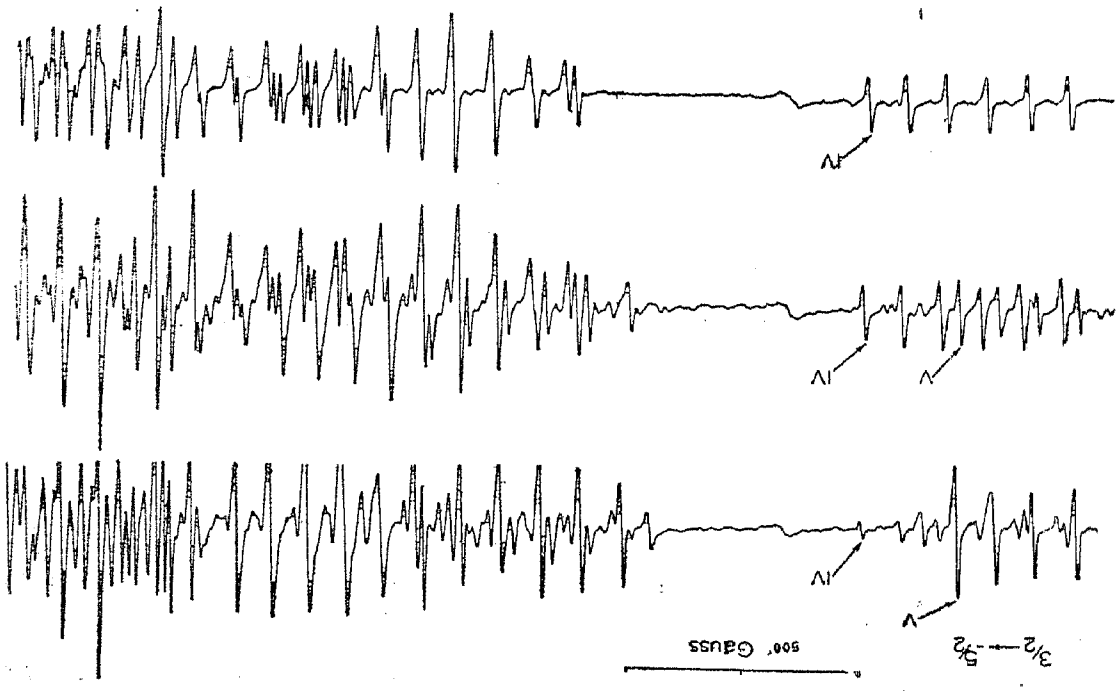

FIG. 3. Exchange of intensities, with time, between the spectra IV and V of Mn^{2+} in NaCl single crystal with H// [001] direction. Only the lower field sides of the spectra are shown.

it is however to be taken as stable when compared to the lifetime of spectrum VII. It is likely this is because that temporarily two vacancies are associated with the complex of spectrum VII while only one vacancy is associated with that of spectrum V. There are however many possibilities for the position of the vacancy or vacancies. The position of the vacancy or vacancies might be such as to increase the crystal field or such as to decrease the crystal field which the Mn^{2+} ion experiences when coupled to O_2^{2-} ion. The crystal field for spectrum V is larger than that for IV while that for VII is smaller. The D values for the spectra V, IV and VII are 588·6, 549·6 and 450 $\pm$ 20 gauss respectively. The explanation given for the origin of the spectra V and VII, though quite probable, is to be taken as tentative.

The effect of temperature on the fine structure spacing of spectrum IV has been measured in the range $-180°$ to 250° C. The dependence of D

as a function of temperature for spectrum IV is shown in Fig. 4. It is approximately represented by

$$|D| = D_0 (1 + bT + cT^2)$$

with $D_0 = (572 \pm 5) \times 10^{-4}$ cm.$^{-1}$, $b = -5{\cdot}0699 \times 10^{-4}$ deg.$^{-1}$, $c = +5{\cdot}7167 \times 10^{-6}$ deg.$^{-2}$ Small changes are also found in other fine structure parameters. However, hyperfine coupling parameter is practically constant with temperature.

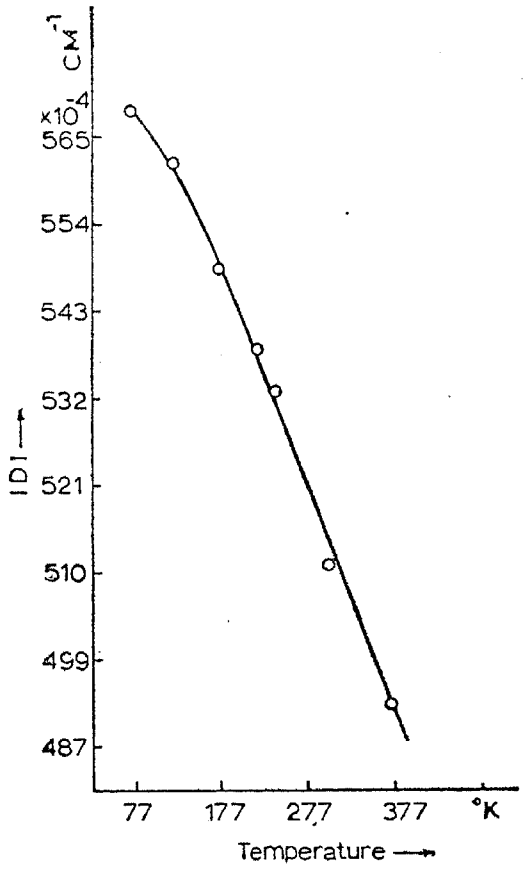

FIG. 4. Variation of fine structure axial crystalline field splitting parameter, D, with temperature for spectrum IV of Mn^{2+} in NaCl.

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