

ELECTRON SPIN RESONANCE OF Mn^{2+} IN NaCl SINGLE CRYSTAL AND LATTICE DEFECTS

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ABSTRACT

The electron spin resonance spectra of Mn^{2+} in NaCl single crystals are investigated in detail. Seven different spectra (I, II, III₁, III₂, IV, V and VI) are observed. The spectra I-IV are the same as those observed by earlier workers, while the spectra V and VI are observed here for the first time. The local symmetry at the paramagnetic ion is orthorhombic for the spectra IV and V and tetragonal for the spectrum VI about the crystallographic [001] direction. The properties of the spectrum IV are explained in terms of an associated pair $Mn^{2+}: O_2^{2-}$ with O_2^{2-} molecular ion at the nearest neighbour anion site in the [001] direction with its internuclear axis in the (001) plane. The spectrum V is assigned to the associated pair $Mn^{2+}: O_2^{2-}$ coupled with a nearby cation vacancy in the [001] direction and the spectrum VI to Mn^{2+} ion associated with OH^- ion at the anion site in the [001] direction with a probable second neighbour cation vacancy. All the observed spectra are analysed in terms of the parameters of the usual spin-Hamiltonian.

INTRODUCTION

INVESTIGATIONS of the spin resonance of Mn^{2+} doped in sodium chloride single crystals have been reported several times in recent years. The introduction of a divalent Mn^{2+} ion causes a charge unbalance. Different charge compensations corresponding to different point symmetries have been reported. Oshima and his coworkers,¹ Forrester and Schneider,² Low³ and Watkins⁴ have all obtained a spectrum (designated I) which consists of a single broad resonance corresponding to precipitated Mn^{2+} ions. Forrester and Schneider,² Low³ and Watkins⁴ have reported also spectrum (II) corresponding to isolated Mn^{2+} ions which are not near any defect and therefore have local cubic symmetry. Morigaki, Fujimoto and Itoh⁵ and Watkins⁴ have recorded an orthorhombic spectrum (III₁) corresponding to Mn^{2+} ions associated with nearest neighbour cation vacancies. Watkins⁴ has found a tetragonal spectrum (III₂) due to Mn^{2+} ions associated with a second nearest neighbour

cation vacancy. Watkins⁴ as well as Yokozawa and Kazumata⁶ have found a spectrum IV showing orthorhombic symmetry which was assigned by them to an associated pair Mn²⁺: X²⁻ where X²⁻ is an unknown impurity at the nearest anion site. The present experiments reveal two additional spectra (V and VI). This paper deals with an analysis of all the observed spectra (I-VI) along with a discussion regarding their origin in terms of the possible lattice defects. The variation of the intensities and the observation of the so-called forbidden transitions with $\Delta m = \pm 1$ will be discussed in a later paper.⁷

EXPERIMENTAL PROCEDURE

All the crystals were grown from melt by using a procedure based upon the Stockbarger's⁸ modification of Bridgman's technique. E. Merck's guaranteed reagents were used and doping was done by mixing manganous chloride and sodium chloride powders before melting.

A Varian X-band spectrometer V4502-12 with 100 Kc./sec. field modulation was used. The field was calculated accurately by measuring the frequency of proton resonance with a Hewlett Packard frequency counter HP 524C. Diphenyl picryl hydrazil for which $g = 2.0036$ was used as a field marker.

THEORY

The ground state of Mn²⁺ ion $3d^5$, $^6S_{5/2}$ in a crystalline field is described by the spin Hamiltonian.⁹

$$\begin{aligned}
 H = & g\beta H \cdot S + D \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\} + E (S_x^2 - S_y^2) \\
 & + \frac{a}{6} \left[S_1^4 + S_2^4 + S_3^4 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1) \right] \\
 & + S \cdot A \cdot I - \gamma\beta_n H \cdot I + Q' \left\{ I_z^2 - \frac{1}{3} I(I+1) \right\}.
 \end{aligned}$$

Here g is the spectroscopic splitting factor, β is the Bohr magneton, H the external magnetic field, S the electron spin operator and D is the axial field splitting parameter. The departures from the axial symmetry are taken into account by the parameter E . a is the cubic field splitting constant where $3a$ gives the separation between the doublet and the quartet that will be present when the symmetry is cubic and no magnetic field is applied. A is the hyper-

fine coupling constant. The terms involving γ and Q' account for the interaction of the nuclear spin I with the external magnetic field and the nuclear electric quadrupole moment respectively. They are very small in magnitude and will therefore be neglected here. However, they will be included in the analysis of forbidden $\Delta m = \pm 1$ transitions in a later paper.⁷

The resonance fields for the allowed $\Delta M = \pm 1$, $\Delta m = 0$ transitions are^{5, 9, 10}

$$H = H_0 - Km - \frac{A^2}{2H_0} [I(I+1) - m^2 + m(2M-1)] \\ + f_{M \rightarrow M-1}(D, E, a)$$

$$K^2 = A_x^2 n_x^2 + A_y^2 n_y^2 + A_z^2 n_z^2, \quad H_0 = \frac{h\nu}{g\beta}$$

where H is the magnetic field at which the transition is observed, ν is the microwave frequency

and

$$f_{\pm 5/2 \rightleftharpoons \pm 3/2}(D, E, a) \\ = \mp 2D(3n_z^2 - 1) \mp 6E(n_x^2 - n_y^2) \\ + \frac{1}{H_0} [D^2(1 - n_z^2)(1 - 33n_z^2) \\ + E^2\{36n_z^2 + 33(n_x^2 - n_y^2) - 32\} \\ + 2DE(n_x^2 - n_y^2)(1 + 33n_z^2)] \\ \mp 2pa$$

$$f_{\pm 3/2 \rightleftharpoons \pm 1/2}(D, E, a) \\ = \mp D(3n_z^2 - 1) \mp 3E(n_x^2 - n_y^2) \\ + \frac{1}{4H_0} [D^2(1 - n_z^2)(21n_z^2 - 5) + E^2\{16 - 36n_z^2 \\ - 21(n_x^2 - n_y^2)^2\} - 2DE(n_x^2 - n_y^2)(21n_z^2 + 5)] \\ \pm \frac{5}{2}pa$$

$$\begin{aligned}
 & f+1/2 \rightarrow -1/2 (D, E, a) \\
 & = \frac{2}{H_0} [D^2 (1 - n_z^2) (9n_z^2 - 1) + E^2 \{8 - 12 n_z^2 \\
 & \quad - 9 (n_x^2 - n_y^2)^2\} - 2DE (n_x^2 - n_y^2) (9n_z^2 - 1)]
 \end{aligned}$$

where M and m are the electronic and nuclear magnetic quantum numbers and $p = 1-5 (n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)$; n_x, n_y, n_z are the direction cosines of the external magnetic field with respect to x, y, z axes while n_1, n_2, n_3 are the same with respect to cubic co-ordinate axes 1, 2, 3. For the spectrum III₁ the axes x, y, z and 1, 2, 3 are rotated through an angle of 45° in a (100) plane while for all the other spectra they coincide.

RESULTS AND INTERPRETATION

The occurrence of the different charge compensation mechanisms is dependent upon many factors associated with the total crystal growth process and the impurity concentration. In the crystals of comparatively high manganese ion concentration (when about 10⁻³ mole fraction of MnCl₂ is added to the melt) only a single broad line (spectrum I) is found and this broad line can be resolved into a complicated structure on quenching the crystal. If the manganese ion concentration is low a partially resolved fine structure superimposed on a broad resonance is obtained and this is further resolved on quenching the crystal. The spectra I, II and III are easily identified in this structure. The quenched crystals grown in vacuum show only the spectra I, II and III. However, when the melt is exposed to the atmosphere for a couple of hours before lowering in the temperature gradient, the spectrum IV appears faintly in some crystals along with spectra I, II and III. Longer exposure of the melt to the atmosphere sometimes gave crystals which did not show any trace of the spectra I, III but showed an intense spectrum IV accompanied by a weak spectrum VI. It was also possible to obtain some other times crystals which show spectra IV and V with either some traces of spectra I and II alone or some traces of all the spectra I, II and III. It was found that the spectrum VI disappears by quenching the crystal while the relative intensities of the spectra IV and V get affected by quenching in case both are present. It is found that the intensities of all the spectra (III-VI) fall off very rapidly when the magnetic field direction deviates from the corresponding symmetry axes. Some of the spectra observed are shown in Figs. 1 and 2. Crystals showing spectra IV and VI showed only spectrum IV after quenching and the spectrum IV did not change at all after further quenching or after many months. This points out that while there is a considerable

effect of quenching on spectra I, II, III, V and VI, there is no effect of quenching on spectrum IV. The observed effect of quenching on spectra I, II and III is in line with the models suggested by earlier workers for these spectra. The spectra II and III are discussed in detail by Watkins.⁴ Our values of the parameters of the spin Hamiltonian are given in Table I, and these agree fairly well with those obtained by earlier workers. Spectrum IV was assigned by earlier workers to an associated pair $Mn^{2+} : X^{2-}$ where X^{2-} is an impurity like O^{2-} , S^{2-} , etc., that occupied a nearest neighbour anion site. As spectrum IV could not be obtained in crystals grown in vacuum and the intensity of the spectrum IV increases with the time of exposure of the melt to the atmosphere it is reasonable to expect that oxygen is involved in the model. The spectrum IV showed an orthorhombic symmetry which is evident from the presence of the E term in the analysis. If the model involved is an atomic oxygen ion (O^{2-}) in the [001] direction of the crystal, it is difficult to understand the observed orthorhombic symmetry along that direction. Earlier workers tried to understand this by suggesting that the axis of symmetry is probably slightly tilted from the [001] direction because of either a nearby anion vacancy in the [100] or [110] direction or because of a radical (OH^-) associated to the $Mn : X^{2-}$ model. However, if a vacancy is involved in the model one expects an effect of temperature on the spectrum IV because vacancies are expected to be disturbed easily by temperature or quenching and because spectra III whose models involve vacancies are observed to be effected by temperature and quenching. As spectrum IV is not so affected, it appears that its model will not have any thing to do with the vacancies. The model of the spectrum does not probably have any association with (OH^-) as (OH^-) is expected to get affected by quenching while this spectrum is not. It appears reasonable to assume that the spectrum IV is due to an associated pair $Mn^{2+} : O_2^{2-}$ with the molecular ion O_2^{2-} in place of the nearest neighbour halogen ion in the [001] direction. The existence of the orthorhombic symmetry along the [001] direction suggests that the internuclear axis of the molecular ion is in the (001) plane in which case the molecular ion will exhibit a C_2 symmetry along the [001] direction as required by the analysis. The constants of the spin Hamiltonian obtained from the analysis are given in Table I and they agree fairly well with those obtained by Watkins.

Analysis of the spectrum V, reveals orthorhombic symmetry along the [001] direction of the crystal like the spectrum IV and it is obtained only in crystals whose melts were exposed to air. However, one finds that the intensity of this spectrum gets affected by quenching and also changes with time like the spectra III. This suggests that spectrum V is very likely due to

TABLE I
Spin-Hamiltonian Parameters for Mn^{2+} : NaCl at $\sim 20^\circ C$.

Designation	g	A $\times 10^{-4} \text{ cm.}^{-1}$	D $\times 10^{-4} \text{ cm.}^{-1}$	E $\times 10^{-4} \text{ cm.}^{-1}$	a $\times 10^{-4} \text{ cm.}^{-1}$	References
I	~ 2.014	1, 2, 3, 4 and present work
II	2.0019 ± 0.001	-82.22	-1	2, 3, 4 and present work
III ₁	2.0021 ± 0.002	$A_x = -82.92$ $A_y = A_z = -82.61$	-135.0	40.6	-1.2	4, 5 and present work
III ₂	2.0022 ± 0.002	-80.6	$+131.0$	4 and present work
IV	2.0017 ± 0.002	$A_x = -78.76$ $A_y = -80.42$ $A_z = -78.43$	-511.0	20.0	..	4, 6 and present work
V	1.9878 ± 0.002	$A_x = -79.25$ $A_y = A_z = -79.47$	-550.10	92.75	$+1.67$	Present work
VI	2.0085 ± 0.002	-77.78	$+627.99$..	$+1.7$	Present work

an associated pair Mn²⁺: O₂²⁻ like the model responsible for spectrum IV but in addition has a second neighbour cation vacancy in the [001] direction, further associated to the model. The existence of this associated vacancy with the model Mn²⁺: O₂²⁻ explains the larger D and E values because of its influence on the electron cloud of the molecular ion O₂²⁻.

Spectrum VI reveals a tetragonal symmetry along [001] direction and it disappears after quenching. This is likely due to Mn²⁺ ion associated with a point defect in which a nearest Cl⁻ ion is replaced by an OH⁻ ion. It is not yet clear whether this model is further associated with a second neighbour anion vacancy in the [001] direction or not. With repeated heat treatment or quenching the crystal the OH⁻ ions dissociate resulting in the disappearance of the spectrum VI. The presence of such OH⁻ ions in most of the synthetic crystals of alkali halides has been found by Rolfe¹¹ and Etzel and Patterson¹² in optical absorption and the dissociation of these ions has been studied by Sierro.^{13, 14} The O-H axis in the OH⁻ ion should be along [001] axis to be consistent with a vanishing E value. The analysis is presented in Table I. It is to be noted that the assignments of the spectrum IV to Mn²⁺: O₂²⁻ the spectrum V to the associated pair involving O₂²⁻ molar ion and a vacancy and the spectrum VI to the associated pair involving OH⁻ are all to be taken as likely but tentative and one has to get further confirmation in this connection.

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REFERENCES

1. Oshima, K., Abe, H., Nagano, H. and Nagusa, M. *J. Chem. Phys.*, 1955, **23**, 1721.
Abe, H., Nagano, H., Nagusa, M. and Oshima, K. *Ibid.*, 1956, **25**, 378.
2. Forrester, P. A. and Schneider, E. E. *Proc. Phys. Soc.*, 1956, **69 B**, 833.
3. Low, W. *.. Ibid.*, 1956, **69 B**, 837.

4. Watkins, G. D. .. *Phys. Rev.*, 1959, **113**, 79 (and references therein).
5. Morigaki, K., Fujimoto, M. and Itoh, J. *J. Phys. Soc., Japan*, 1958, **13**, 1174.
6. Yokozawa, Y. and Kazumata, Y. *Ibid.*, 1961, **16**, 694.
7. Shrivastava, K. N. and Venkateswarlu, P. To be published in *Proc. Indian Acad. Sci.*
8. Stockbarger, D. C. .. *Rev. Sci. Instru.*, 1956, **7**, 133.
9. Bleaney, B. and Ingram, D. J. E. *Proc. Roy. Soc.*, 1951, **205 A**, 336.
10. ——— .. *Phil. Mag.*, 1951, **42**, 441.
11. Rolfe, J. .. *Phys. Rev. Letters*, 1958, **7**, 56.
12. Etzel, H. W. and Patterson, D. *Phys. Rev.*, 1958, **112**, 1112.
13. Sierro, J. .. *J. Chem. Phys.*, 1961, **34**, 2183.
14. ——— .. *Phys. Letters*, 1963, **4**, 178.