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EPR of Mn^{2+} in $Na_2ZnCl_4 . 3H_2O$

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Abstract. The EPR zero-field splitting parameter D of the Mn^{2+} ion in $Na_2ZnCl_4.3H_2O$ has been studied theoretically. A comparison between the measured values and the data calculated using the previous model of the Mn^{2+} ion's environment in $Na_2ZnCl_4.3H_2O$ shows that this model seems to be unsuccessful for investigating the EPR parameter. A new model of the environment of Mn^{2+} has been proposed and appears to be reasonable.

1. Introduction

The hexagonal unimolecular unit cell of the $Na_2ZnCl_4 . 3H_2O$ crystal is described by the point group P31m with lattice parameters $a = 6.876$ and $c = 5.955$ Å (Brehler 1960, Weiss and Wust 1973). The Mn^{2+} impurity ions occupy the Zn^{2+} sites in $Na_2ZnCl_4 . 3H_2O$ (Schlaak and Weiss 1973, Lukin *et al* 1981), surrounded by trigonally distorted tetrahedrons (distorted by about 2.25°) with symmetry C_{3v} (figure 1). The $Na_2ZnCl_4 . 3H_2O$ single crystals were grown from a saturated solution containing NaCl and $ZnCl_2$. The Mn^{2+} impurity ions were added as $MnCl_2 . 6H_2O$. The manganese impurity ion concentration in the crystal was less than 0.1% (Schlaak and Weiss 1973, Lukin *et al* 1983, Lukin and Teslya 1986).

The EPR zero-field splitting parameter D ($\approx -900 \times 10^{-4}\,\mathrm{cm}^{-1}$) has been reported by many authors (Abrabams and Bernstein 1966, Schlaak and Weiss 1973, Lukin *et al* 1981, 1983, Lukin and Teslya 1986). But their theoretical investigations, which were all based on the spin–orbit coupling mechanism, encountered a difficulty because a large value of D was not obtained for the Mn^{2+} ion in structures slightly distorted from the tetrahedron. To explain this value of D, the following assumptions were proposed.

(*a*) The D value of Mn^{2+} in $Na_2ZnCl_4 . 3H_2O$ is due to the contributions of various mechanisms (Schlaak and Weiss 1973);

(*b*) the large value of D is probably due to the change of sign of the distortion of the immediate environment from stretching to compression, and the change takes place only when the Zn^{2+} ion in the $Na_2ZnCl_4 . 3H_2O$ is replaced by Mn^{2+} (Lukin *et al* 1983, Lukin and Teslya 1986).

It is well known that the EPR method has been widely used to obtain valuable information about the structure of impurities in crystal lattices (see, e.g., Siegel and Müller 1979a, b, Bykov *et al* 1980, 1983, Sangster 1981, Ribeiro *et al* 1982, Snnanadana

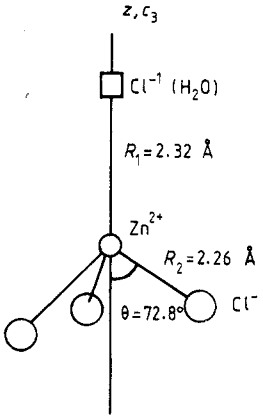

Figure 1. Model of Zn^{2+} (Mn^{2+}) centre in $Na_2ZnCl_4.3H_2O$. □, Cl^- for model I, H_2O for model II.

and Jagannathan 1984, Müller *et al* 1985, Malovichko *et al* 1986, Zhou 1987, Yu and Zhao 1988).

In this paper we first deduce from the above assumptions that the previous model (I), in which the Mn^{2+} centre is associated with an incorporated $(MnCl_4)^{2-}$ complex, seems to be unsuccessful in explaining the EPR parameter. Second, using some previous work for reference, we propose a new model (II) in which the Mn^{2+} centre is associated with the incorporated $(MnCl_3H_2O)^-$ complex and verify it.

2. Theoretical formulae

2.1. Spin–orbit coupling mechanism

A number of mechanisms have been suggested to contribute to the EPR parameters of ^6S (d^5) state ions in crystals. The spin–orbit (SO) coupling mechanism describes the combined effect of the SO interaction and the crystal field. This can be divided into two parts: one resulting from an inter-term interaction and the other describing the effect arising in a pure d^5 configuration. The first part can be evaluated using the theory of Orbach *et al* (1965) and will be considered in § 2.2. Most important is the second part, which can be evaluated by employing the Blume–Orbach (1962) perturbation procedure or the Yu–Zhao (1984, 1986) and Yu *et al* (1985) procedure. In trigonal symmetry, the EPR zero-field splitting parameter D is expressed as

$$D_{\mathrm{SO}} = -\frac{3\zeta^2}{70E(\mathrm{P})^2E(\mathrm{D})}(B_{20}^2 + 21\zeta B_{20}) + \frac{\zeta^2}{126E(\mathrm{P})^2E(\mathrm{G})}(-10B_{40}^2 + 7B_{43}^2) \qquad (1)$$

where

$$\begin{aligned} E(\mathrm{P}) &= (E^4\mathrm{P}) - E(^6\mathrm{S}) = 7B + 7C + 2\alpha + 2\beta \\ E(\mathrm{D}) &= E(^4\mathrm{D}) - E(^6\mathrm{S}) = 17B + 5C + 6\alpha \qquad (2) \\ E(\mathrm{G}) &= E(^4\mathrm{G}) - E(^6\mathrm{S}) = 10B + 5C + 20\alpha \end{aligned}$$

and B_{mn} are the crystal field parameters obtained from (Lever 1968)

$$V_{\text{cryst}} = \sum_{imn} A_n^m r_i^m C_n^m(\theta_i, \varphi_i)$$
$$C_n^m(\theta, \varphi) = [4\pi/(2m+1)]^{1/2} Y_{mn}(\theta, \varphi) \qquad B_{mn} = A_n^m \langle r^m \rangle. \tag{3}$$

By considering the covalency effect and introducing the average covalency parameter N (Zhao and Zhang 1983), the Racah parameters B and C, the Racah and Trees correction parameters α and β and the spin–orbit coupling parameter ζ can be written

$$B = N^4 B_0 \qquad C = N^4 C_0 \qquad \alpha = N^4 \alpha_0 \qquad \beta = N^4 \beta_0 \qquad \zeta = N^2 \zeta_0. \tag{4}$$

where the subscript 0 indicates free-ion values. From figure 1, the crystal field parameters B_{mn} are given by (Pauling 1960)

$$B_{20} = -[N_1^2 q_1/R_1^3 + \tfrac{3}{2} N_2^2 q_2 (3\cos\theta - 1)/R_2^3] e\langle r^2 \rangle_0$$
$$B_{40} = -[N_1^2 q_1/R_1^5 + \tfrac{3}{8} N_2^2 q_2 (35\cos^4\theta - 30\cos^2\theta + 3)/R_2^5] e\langle r^4 \rangle_0 \tag{5}$$
$$B_{43} = [-\tfrac{3}{4} N_2^2 q_2 \sqrt{35}(\sin^3\theta \cos\theta)/R_2^5] e\langle r^4 \rangle_0$$

where q refers to the charge of a ligand (Blume and Orbach 1962). In the above expressions values have been calculated (Zhao *et al* 1982) for Mn^{2+}: $B_0 = 911\ \text{cm}^{-1}$, $C_0 = 3273\ \text{cm}^{-1}$, $\zeta_0 = 337\ \text{cm}^{-1}$, $\alpha_0 = 65\ \text{cm}^{-1}$, $\beta_0 = -131\ \text{cm}^{-1}$, $\langle r^2 \rangle_0 = 2.7755$ au and $\langle r^4 \rangle_0 = 23.2954$ au. The values can also be fitted approximately by Pauling's (1960) method: $N \approx 0.9$ for a Mn^{2+}–O^{2-} bond and $N \approx 0.8$ for a Mn^{2+}–Cl^- bond.

2.2. *Other mechanisms*

Orbach *et al* (1965) and Sharman *et al* (1966, 1967, 1968) (see also Gordy and Thomas 1956) investigated in detail the effect of inter-term interactions through the spin–orbit coupling. They called this effect the ODS mechanism. The spin–spin interaction (SS) was first suggested by Pryce (1950) to contribute to the EPR parameter D of ^6S (d^5) ions (see also Lukin *et al* 1981). This mechanism was studied in detail for the Mn^{2+} ion by Sharman *et al* (1966, 1967, 1968). The relativistic mechanism (R) (Wybourne 1965, Van Heuvelen 1967) was discussed in detail for the Mn^{2+} ion in a fourfold coordination tetrahedron by Edgar *et al* (1980) (see also Matumura 1959, Malovichko *et al* 1986). Recently, Yu *et al* (1985) suggested the combined effects of the spin–spin and spin–orbit couplings (SS–SO) (Orbach *et al* 1965). All these mechanisms can be expressed as functions of parameters A_n^m or B_{mn} in equations (3) and (5).

In addition, the contribution of lattice vibrations by the parameter D in $Na_2ZnCl_4.3H_2O$:Mn^{2+} was investigated by Schlaak and Weiss (1973) and a value $D_V \approx 120 \times 10^{-4}\ \text{cm}^{-1}$ was obtained (see also Ribeiro *et al* 1982).

3. Study using model I

In this model (Sharman *et al* 1966, 1967, 1968), the Mn^{2+} ion coordinated by four fluorines is associated with an incorporated $(MnCl_4)^{2-}$ complex (Siegel and Müller 1979a, b) (figure 1). Consequently (Simanek and Müller 1970), in equations (4) and (5) the parameters $N = N_1 = N_2 = 0.8$ for the Mn^{2+}–Cl^- bond and $q_1 = q_2 = -e$ for a ligand

Table 1. Various contributions to D (in 10^{-4} cm^{-1}).

Mechanism	Model I	Model II
SO	−7.0	−1062.8
ODS	0.8	34.5
SS	−2.7	18.1
R	8.8	−59.4
SS–SO	−8.6	47.0
V	120	120
Total	113.2	−902.6
Experiment	−901[a] −943[b]	

[a] Schlaak and Weiss (1973).
[b] Lukin *et al* (1983), Lukin and Teslya (1986).

Cl^- are taken, and the contributions of the various mechanism to the EPR parameter D are as listed in table 1. The calculated value $D = 111.2 \times 10^{-4}$ cm^{-1} does not agree with $D \approx -900 \times 10^{-4}$ cm^{-1} measured earlier (Schlaak and Weiss 1973, Lukin *et al* 1983, Lukin and Teslya 1986), either in magnitude or, more significantly, in sign. This shows clearly that the first assumption in § 1, that the D value in $Na_2ZnCl_4.3H_2O:Mn^{2+}$ is due to the contributions from various mechanisms seems to be unreasonable in model I.

To check the second assumption in § 1 (Freeman and Pilbrow 1974), we calculate the dependence of the parameter D_{SO} on bond length R as shown in figure 2. From figure 2, it is easy to see that the effect of changes in D_{SO} on R_2 are small and a sufficient magnitude for D_{SO} can be obtained from the change in R_1 (Hagen and Trappeniers 1970, 1973, Hannay and Smyth 1946). If contributions from other mechanisms are considered, the magnitude of D_{SO} should be about -1000×10^{-4} cm^{-1}, which corresponds to a bond length $R_1 < 1.9$ Å. Clearly, it seems to be unreasonable that the distortion of the bond length from the host lattice value ($R_1 = 2.32$ Å) is more than 20% when the Zn^{2+} ion in $Na_2ZnCl_4.3H_2O$ is replaced by Mn^{2+} (Matumura 1959), because the valences of the cations Mn^{2+} and Zn^{2+} are identical (Müller *et al* 1985) and their ionic radii are almost the same (0.85 Å and 0.83 Å) (Schlaak and Weiss 1973).

These results show that this model of the environment of the Mn^{2+} ion seems to be unsuccessful for explaining the EPR parameter (Pryce 1950). We must find another model.

4. Analysis of model II

To explain the EPR spectra of the Cr^{3+} ion in the chlorine hydrates NH_4Cl and CsCl (Schlaak and Weiss 1973), Stibbe and Trappeniers (1978) assumed that the Cr^{3+} centre is associated with incorporated $(CrCl_n(H_2O)_{6-n})^{3-n}$ rather than $(CrCl_6)^{3-}$ in the anhydrates NH_4Cl and CsCl, in which the Cl^- ions along the crystal axis z are replaced by H_2O molecules (Snnanadana and Jagannathan 1984). A little earlier, some previous work using a similar method was performed by many other authors (see, e.g., Elving and Zemel 1957, Lever 1968, Hagen and Trappeniers 1970, 1973, Freeman and Pilbrow

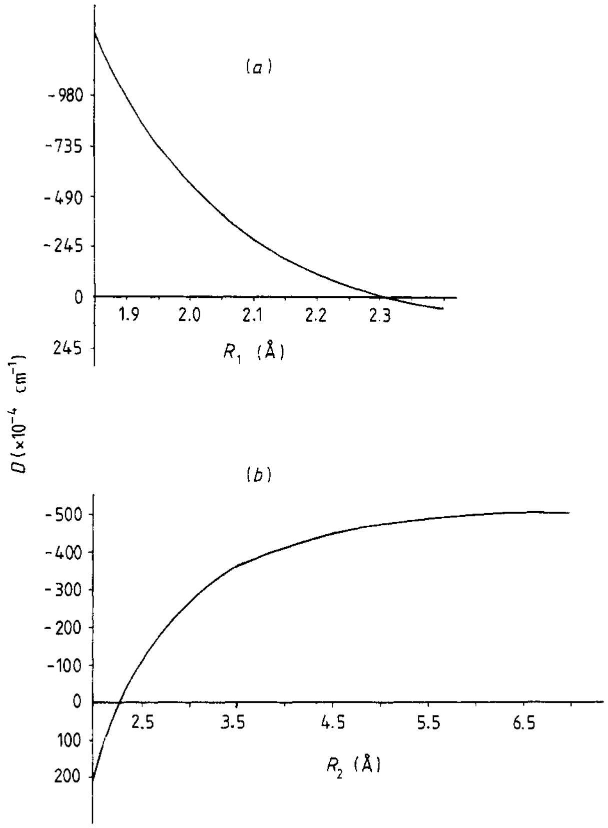

Figure 2. Dependence of D_{SO} on the bond length R: (*a*) $R_2 = 2.26$ Å, $\theta = 72.8°$; (*b*) $R_1 = 2.32$ Å, $\theta = 72.8°$.

1974, Boettcher and Spaeth 1974a, b). With the success of this model for investigating the EPR spectra of Cr^{3+} in the chlorine hydrates NH_4Cl and CsCl, we assume that the Mn^{2+} centre in $Na_2ZnCl_4.3H_2O$ is associated with an incorporated $(MnCl_3(H_2O))^-$ complex rather than $(MnCl_4)^{2-}$ as in model I (Abrabams and Bernstein 1966), one Cl^- ion at the crystal axis z being replaced by one molecule of H_2O (figure 1).

4.1. *Hyperfine splitting constant A*

As was shown (Brehler 1960, Matumura 1959, Simanek and Müller 1970), the hyperfine interaction constant A of Mn^{2+} (Bykov *et al* 1980) depends on the covalency parameter c (usually c is divided by the number, n, of ligands) of the bond between manganese and its neighbours (figure 3). The covalency c is calculated by Hannay and Smyth (1946) as

$$c = 1 - 0.16(X_{Mn} - X_B) - 0.035(X_{Mn} - X_B)^2 \qquad (6)$$

where X_{Mn} and X_B are the electronegativities of the Mn^{2+} ion and the ligand B (Gordy and Thomas 1956). Equation (6) and figure 3 give a simple qualitative method by which Schlaak and Weiss (1973) showed that the hyperfine constant A ($\approx 75 \times 10^{-4}$ cm^{-1}) of Mn^{2+} in $Na_2ZnCl_4.3H_2O$ fits the well established dependence of A on the covalency of

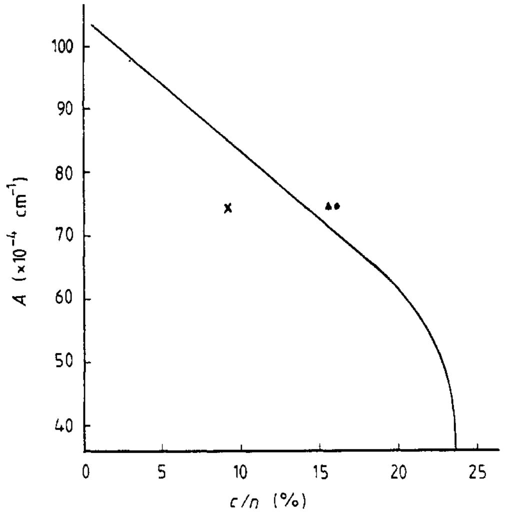

Figure 3. Hyperfine splitting constant A of Mn^{2+} as a function of the covalence of the bond: ●, model I for $Na_2ZnCl_4.3H_2O$:Mn^{2+}; ▲, model II for $Na_2ZnCl_4.3H_2O$: Mn^{2+}; ×, model for Mn^{2+} at a Na^+ site in $Na_2ZnCl_4.3H_2O$.

the bonds of Mn^{2+} in Zn^{2+} sites and is in contrast to the value expected for Mn^{2+} at a Na^+ site (Lukin *et al* 1983), and concluded that the Zn^{2+} is replaced by Mn^{2+} in $Na_2ZnCl_4.3H_2O$. We can use this to test model II. With $X_{Mn} = 1.4$, $X_{Cl} = 3.0$, $X_O = 3.5$ (Gordy and Thomas 1956, Pauling 1960) and $X_B = \frac{1}{4}(3X_{Cl} + X_O) = 3.125$, we get $c/n = 15.5\%$ (close to the 16.2% of model I calculated by Schlaak and Weiss (1973)), as shown in figure 3. It is easy to see from figure 3 that model II seems to be qualitatively reasonable.

4.2. *Zero-field splitting parameter D*

For model II we take $N_1 = 0.9$ and $N_2 = 0.8$ for the Mn^{2+}–O^{2-} and Mn^{2+}–Cl^- bonds, $q_1 = -2e$ and $q_2 = -e$ for O^{2-} and Cl^-, respectively, and $N = \frac{1}{4}(N_1 + 3N_2) = 0.825$ in equations (4) and (5), and the contributions of the various mechanisms to the EPR parameter D are as listed in table 1. The good agreement between the calculated and the measured values of D (Simanek and Müller 1970) shows quantitatively that this model of the Mn^{2+} ion's environment seems to be reasonable.

To further test this model, we calculate the dependence of the parameter D of Mn^{2+} in $Na_2ZnCl_4.3H_2O$ on the axial compression of the crystal in a direction parallel to the symmetry axis of the crystal (trigonal axis of the paramagnetic centre). The calculated value $dD/dP \approx -3.3 \times 10^{-6}\ cm^{-1}\ kbar^{-1}$ is comparable with the measured $dD/dP \approx -1.7 \times 10^{-6}\ cm^{-1}/kb$ (Bykov *et al* 1983). The difference between the calculated value and the experimental one seems to be caused, as pointed out by Lukin *et al* (1983), by considering in the calculation only the linear distance change

$$\begin{aligned} dR_1/dP &= -\sigma_\parallel R_1 \\ dR_2/dP &= R_2(\sigma_\parallel \sin\theta - \sigma_\perp \cos\theta) \end{aligned} \tag{7}$$

(where $\sigma_\parallel = 1.12 \times 10^{-6}\ bar^{-1}$ and $\sigma_\perp = 1.16 \times 10^{-6}\ bar^{-1}$ are the longitudinal and transverse compressibilities of the crystal and $\theta = 72.8°$ is the acute angle between the c_3 axis and the direction from the Mn^{2+} ion to the ligand Cl^- (figure 1)) and neglecting the angular change.

It is easy to see from the analyses in this section that model II seems to be reasonable. But, so far, this structure is not quite clear, probably since the concentration of Mn^{2+} impurity ions in the crystals is too low (Schlaak and Weiss 1973, Lukin *et al* 1983, Lukin and Teslya 1986), and the substitution of the H_2O molecules for the Cl^- ions in hydrates is small (Stibbe and Trappeniers 1978).

5. Conclusion

The previous model of the Mn^{2+} ion's environment in $Na_2ZnCl_4.3H_2O$ in which the Mn^{2+} centre is associated with an incorporated $(MnCl_4)^{2-}$ complex seems to be unsuccessful for investigating the EPR parameter. A new model, in which the Mn^{2+} centre is associated with an incorporated $(MnCl_3(H_2O))^-$ complex, has been assumed and verified to be useful, though its structure is not quite clear as yet.

References

Abrabams S C and Bernstein J L 1966 *Acta Crystallogr.* B **25** 1233
Blume M and Orbach R 1962 *Phys. Rev.* **127** 1587
Boettcher F and Spaeth J M 1974a *Phys. Stat. Solidi* b **61** 465
—— 1974b *Phys. Stat. Solidi* b **62** 65
Brehler B 1960 *Z. Kristallogr.* **114** 66
Bykov I P, Geifman I N, Glinchuk M D and Krulikovski B K 1980 *Sov. Phys.-JETP* **51** 386
Bykov I P, Glinchuk M D, Karmazin A A and Laguta V V 1983 *Sov. Phys.-Solid State* **25** 2063
Edgar A, Siegel E and Urban W 1980 *J. Phys. C: Solid State Phys.* **13** 6649
Elving P J and Zemel B 1957 *J. Am. Chem. Sol.* **79** 1281
Freeman T E and Pilbrow J R 1974 *J. Phys. C: Solid State Phys.* **7** 2365
Gordy W and Thomas W J O 1956 *J. Chem. Phys.* **24** 439
Hagen S H and Trappeniers N J 1970 *Physica* **47** 165
—— 1973 *Physica* **66** 166
Hannay N B and Smyth C F 1946 *J. Am. Chem. Soc.* **68** 171
Lever A B P 1968 *Inorganic Electronic Spectroscopy* (Amsterdam: Elsevier)
Lukin S N, Samsonova G Y, Teslya O P and Tsintsadze G A 1981 *Sov. J. Low Temp. Phys.* **7** 459
Lukin S N and Teslya O P 1986 *Sov. Phys.-Solid State* **28** 154
Lukin S N, Teslya O P and Tsintsadze G A 1983 *Sov. Phys.-Solid State* **25** 620
Malovichko G I, Grachev V G and Lukin S N 1986 *Sov. Phys.-Solid State* **28** 553
Matumura O 1959 *J. Phys. Soc. Japan* **14** 108
Müller K A, Berlinger W and Albers J 1985 *Phys. Rev.* B **32** 5837
Orbach R, Das T P and Sharman R R 1965 *Proc. Int. Conf. on Magnetism, Nottingham* p 330
Pauling L 1960 *The Nature of the Chemical Bond* (New York: Cornell University Press)
Pryce M H L 1950 *Phys. Rev.* **80** 1107
Ribeiro G M, Gonzagu L V, Chaves A S, Gazzinelli R, Blinc R, Cevc P, Prelovsek P and Siliki N I 1982 *Phys. Rev.* B **25** 331
Sangster M J L 1981 *J. Phys. C: Solid State Phys.* **14** 2889
Schlaak M and Weiss A 1973 *Z. Naturf.* **28a** 1932
Sharman R R, Orbach R and Das T P 1966 *Phys. Rev.* **149** 257
—— 1967 *Phys. Rev.* **155** 338
—— 1968 *Phys. Rev.* **171** 378
Siegel E and Müller K A 1979a *Phys. Rev.* B **19** 109
—— 1979b *Phys. Rev.* B **20** 3587
Simanek E and Müller K A 1970 *J. Phys. Chem. Solids* **31** 1027
Snnanadana C S and Jagannathan J M 1984 *Solid State Commun.* **53** 985
Stibbe F S and Trappeniers N J 1978 *Physica* **95B** 81
Van Heuvelen A 1967 *J. Chem. Phys.* **46** 4903

Weiss A and Wust A 1973 *Z. Naturf.* **28a** 1919
Wybourne B G 1965 *J. Chem. Phys.* **43** 4506
Yu W L and Zhao M G 1984 *J. Phys. C: Solid State Phys.* **18** L525
—— 1986 *J. Phys. C: Solid State Phys.* **19** 6761
—— 1988 *Phys. Rev.* B **37** 9254
Yu W L, Zhao M G and Lin Z Q 1985 *J. Phys. C: Solid State Phys.* **18** 1857
Zhao M G, Bai G R and Jin H C 1982 *J. Phys. C: Solid State Phys.* **15** 5959
Zhao M G and Zhang Y F 1983 *IEEE Trans. Magn.* **MAG-19** 1972
Zhou Y Y 1987 *J. Phys. C: Solid State Phys.* **20** 5097