EPR of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$

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The EPR spectrum of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ was investigated in the range $100\ K \leqq T \leqq 300\ K$. The spectrum can be described by a Spin Hamiltonian with axial symmetry. The g factor is anisotropic, $g_{\parallel} = 2.0007 \pm 0.0005$; $g_{\perp} = 2.0030 \pm 0.0005$. The axial crystal field splitting constants are $D = (-901.0 \pm 2.0) \cdot 10^{-4}\ cm^{-1}$, $B = (-5.7 \pm 2.0) \cdot 10^{-4}\ cm^{-1}$. The hyperfine splitting constants $A_{\parallel} = (-74.9 \pm 0.2) \cdot 10^{-4}\ cm^{-1}$ and $A_{\perp} = (-74.2 \pm 0.2) \cdot 10^{-4}\ cm^{-1}$ have been determined. This corresponds to a Mn^{2+} ion bond to four Cl^- ions within a tetrahedron. Since a large crystal field splitting constant D is observed, a strong axial crystal field at the site of the Mn^{2+} ion is assumed. From the temperature dependence of the crystal field splitting constant D a dominant phonon frequency of $(117 \pm 10) \cdot 10^{11}\ sec^{-1}$ is deduced.

Introduction

In a preceding paper[1] (in the following I), the crystal structure determination of $Na_2ZnCl_4 \cdot 3\,H_2O$ and of $Na_2ZnCl_4 \cdot 3\,D_2O$ was complemented by the results of ^1H- and ^2H-NMR experiments. Furthermore, information has been gained from ^2H-, ^{23}Na-, ^{35}Cl-, and ^{37}Cl-NMR about the internal fields in these systems[1, 2]. From EPR measurements of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ additional information about the crystal field and the bond character is expected.

Single crystals of $Na_2ZnCl_4 \cdot 3\,H_2O$ were grown from a saturated liquid solution of appropriate composition[1]. Up to 10 mole% $MnCl_2$ were added to the solution. The crystals grown from this reddish solution were visibly uncolored. Sometimes small regions showing the color of the solution could be detected within the crystals. These regions are inclusions within the single crystals containing liquid solution[1]. Confirmation of this was obtained through the EPR measurements, which revealed two Mn^{2+} spectra in these crystals. One spectrum is assigned to Mn^{2+} in liquid solution, the other to Mn^{2+} in a strong electric crystal field (Figure 1). The second spectrum is of weak intensity, indicating the incorporation of only small amounts (probably $\lesssim$ 1 mole‰) of Mn^{2+} at lattice sites within the crystal.

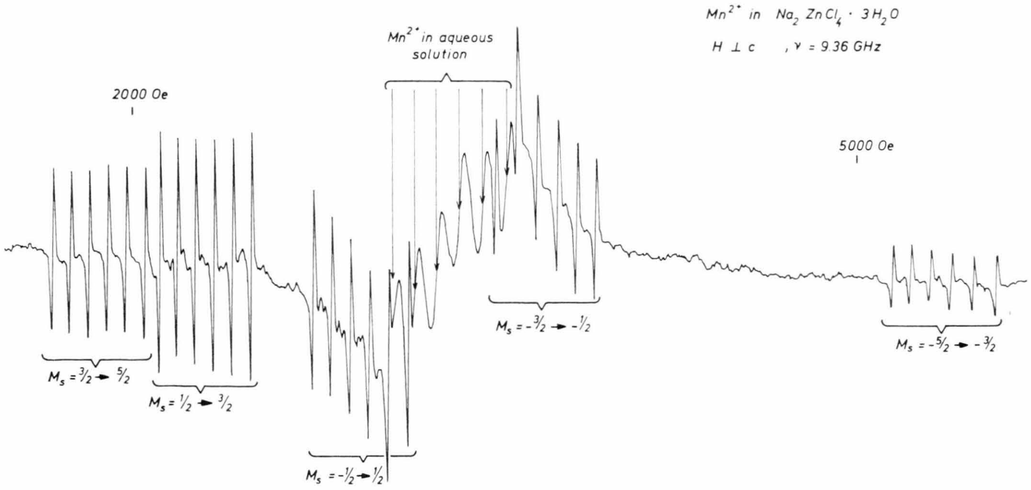

Fig. 1. EPR spectrum of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$. The six wide resonance lines at $g = 2.00$ are due to inclusions of solution containing Mn^{2+}. H is perpendicular to the axis [001] of the crystal.

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Experimental

For the EPR measurements an AEG-20X spectrometer was used. The klystron frequency was measured directly with a Hewlett Packard digital counter via a microwave frequency converter and the magnetic field was determined with an AEG-proton-resonance unit. The maximum error in the determination of the resonance fields is estimated to be ± 2 Oe.

A single crystal of $Na_2ZnCl_4 \cdot 3\,H_2O$ doped with Mn^{2+} was fixed to a goniometer head and optically adjusted with the aid of an optical two circle goniometer[3]. By these means the axis [001] of the crystal was adjusted parallel to the rotation axis of the goniometer head. Then the goniometer head was fixed on the EPR cavity and could be rotated about its axis. Rotating the crystal about the axis [001], the external magnetic field H rotates within the plane (001) of the hexagonal crystal. The EPR spectrum of Mn^{2+} for $[001] \perp H$ was found to be independent of angle.

In a second experiment the crystal was adjusted as described above, but with a crystal axis perpendicular to [001] as axis of rotation. A strong angular dependence of the Mn^{2+} spectrum was found as function of the angle between [001] and H. Maximum splitting of the EPR fine structure splitting occurs for $H \parallel [001]$.

The error in the adjustment of the crystal is estimated to be 1 – 2 degrees. Often the surfaces of the crystal had been affected by air humidity[1] and the optical reflections from these surfaces were opaque. If H is neither parallel nor perpendicular to [001], the intensity of the "allowed" transitions ($\Delta M_S = \pm 1$, $\Delta m_I = 0$) diminishes and is at some angles even weaker than the intensity of the "forbidden" transitions ($\Delta M_S = \pm 1$, $\Delta m_I \neq 0$). Therefore, it was impossible to find the complete angular dependence of the spectrum in the range $0° \leqq \Theta \leqq 90°$. Bleaney and Rubins[4] have treated the angular dependence of the intensity, both of the "forbidden" and the "allowed" transitions.

To gain more information, the temperature dependence of the Mn^{2+}-EPR spectrum of $Na_2ZnCl_4 \cdot 3\,H_2O : Mn^{2+}$ was measured in the range $100\,K \leqq T \leqq 300\,K$ for the special position of $H \parallel [001]$. An AEG variable temperature accessory was used for this experiment.

Results

The EPR spectrum of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ shows axial symmetry as expected from crystal structure considerations. The axis of symmetry is identical with the axis [001] of the crystal. Within the limits of error, there is no angular dependence of the Mn^{2+} spectrum if H rotates in the plane (001) of the crystal. The angular dependence of the Mn^{2+}-EPR spectrum corresponds to a C_3 symmetry of the crystal field. The appropriate Spin Hamiltonian to describe an EPR spectrum with this symmetry is:

$$\begin{aligned}\mathcal{H} = {} & g_{\parallel}\,\mu_B H_z S_z + g_{\perp}\,\mu_B (H_x S_x + H_y S_y) \\ & + D[S_z^2 - \tfrac{1}{3} S(S+1)] + B[35\,S_z^4 \\ & - \{30\,S(S+1) - 25\}\,S_z^2 - 6\,S(S+1) \\ & + 3\,S^2(S+1)^2] + A_{\parallel}\,S_z I_z + A_{\perp}\,(S_x I_x + S_y I_y)\,.\end{aligned} \tag{1}$$

μ_B is the Bohr magneton, H the static magnetic field with its components in x, y, z (z-axis $\triangleq$ c-axis of the crystal), S is the electron spin of Mn^{2+} ($S = 5/2$), and I is the nuclear spin of Mn^{2+} ($I = 5/2$), both S and I given in components in x, y, z. $g_{\parallel}$ and $g_{\perp}$ are the g-factors for $H \parallel [001]$ and for $H \perp [001]$. D and B are axial crystal field splitting constants. $A_{\parallel}$ and $A_{\perp}$ describe the hyperfine splitting parallel to [001] and perpendicular to [001].

Applying this Hamiltonian to the Mn^{2+} spectrum in $Na_2ZnCl_4 \cdot 3\,H_2O$, the parameters of the Hamiltonian can be determined. To do so, a parameter fitting program *, which solves the complete energy matrix by the Jacobi method, was used[3]. To gain a good fitting of the measured resonance fields for $H \parallel [001]$, the angle Θ had to be varied too, resulting in $\Theta = 2.25°$. This shows that the crystal was not perfectly adjusted with the axis [001] perpendicular to the rotation axis of the goniometer, but was squared off by 2.25°.

Assuming the hyperfine splitting constant A to be negative, the signs of the other parameters of the Hamiltonian are fixed too. For $T = 20\,°C$ the values are:

$$\begin{aligned} & g_{\parallel} = 2.0007 \pm 5, \quad g_{\perp} = 2.0030 \pm 5, \\ & D = (-901.0 \pm 2.0) \cdot 10^{-4}\,\mathrm{cm}^{-1} \\ & \qquad \triangleq (-964.6 \pm 2.0)\ \mathrm{Oe}, \\ & B = (-5.7 \pm 2.0) \cdot 10^{-4}\,\mathrm{cm}^{-1} \\ & \qquad \triangleq (-6.1 \pm 2.0)\ \mathrm{Oe}, \end{aligned}$$

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* This program is a modification of the IBM program QCPE 69 of H. H. Gladney (Library of the "Deutsches Rechenzentrum," *D-6100 Darmstadt*).

$$A_{\|} = (-74.9 \pm 0.2) \cdot 10^{-4}\,\mathrm{cm}^{-1} \mathrel{\hat{=}} (-80.2 \pm 0.2)\ \mathrm{Oe},$$
$$A_{\perp} = (-74.2 \pm 0.2) \cdot 10^{-4}\,\mathrm{cm}^{-1} \mathrel{\hat{=}} (-79.4 \pm 0.2)\ \mathrm{Oe}.$$

At the measured field H the differences between the energy $h\nu$ given by the klystron frequency ν and $(E_{M_S} - E_{M_{S-1}})$ calculated with the given parameters of the Hamiltonian correspond to the errors in the determination of the resonance fields (± 2 Oe).

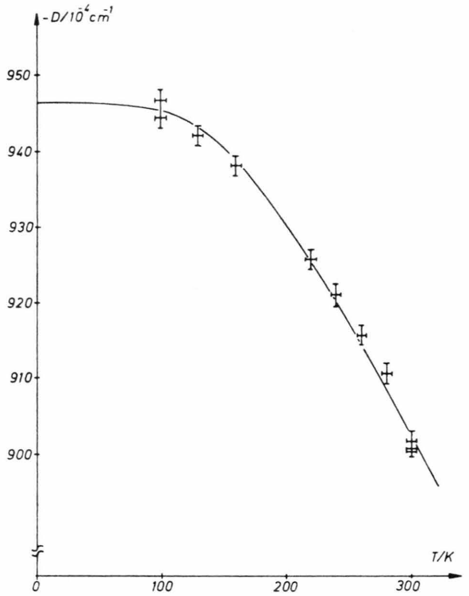

Fig. 2. Temperature dependence of the axial crystal field splitting constant D for Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$, as calculated by Equation (3).

Figure 2 shows the temperature dependence of the axial crystal field splitting constant D. The values $D = D(T)$ have been determined by solving the complete energy matrix as described above. In our experiment, within the limits of error, only the axial crystal field parameter D changed with temperature. The other parameters are independent of T within the following limits: $g_{\|} = 2.001 \pm 0.001$, $A_{\|} = (-74.9 \pm 0.8) \times 10^{-4}\,\mathrm{cm}^{-1}$, $B = (-5.7 \pm 4.0) \times 10^{-4}\,\mathrm{cm}^{-1}$.

Discussion

a) The Location of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$

The crystal structure of $Na_2ZnCl_4 \cdot 3\,H_2O$ is sketched in Figure 3. The atomic coordinates are given in I.

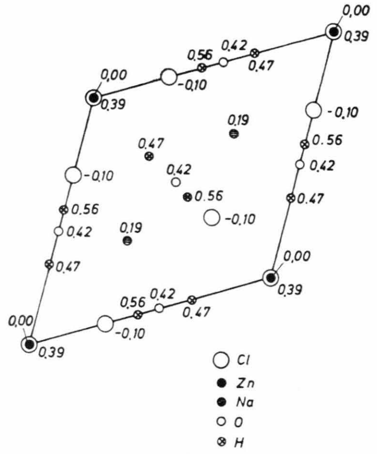

Fig. 3. Projection of the structure of $Na_2ZnCl_4 \cdot 3\,H_2O$ on the plane (001). The z parameter in the figure are approximate [1, 24].

To locate the Mn^{2+} ion within the unit cell of $Na_2ZnCl_4 \cdot 3\,H_2O$, we shall discuss the following arguments:

1. Uniform charge distribution favors a Mn^{2+} ion at a Zn^{2+} ion site.
2. The ionic radii of the cations Mn^{2+}, Zn^{2+}, and Na^+ are in a tetrahedral (octahedral) coordination: 0.85 (0.91) Å, 0.78 (0.83) Å, 0.93 (0.98) Å, respectively. In both coordinations Mn^{2+} is larger than Zn^{2+}, but smaller than Na^+. It can be assumed that an ion rather substitutes another ion having a larger volume than an ion having a smaller one. Thus the ionic radii favor a substitution of the Mn^{2+} ion at the Na^+ sites.
3. The Mn^{2+} EPR spectrum has C_3 symmetry. The Na^+ ion and the Zn^{2+} ion are located at crystal sites with symmetry 3 and 3 m, respectively. The lattice sites of H_2O and of the interstitial sites are of lower symmetry. Therefore, from the symmetry of the EPR spectrum we conclude that Mn^{2+} is either at a Na^{2+} site or at a Zn^{2+} site.
4. As shown below, the hyperfine constant A of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ fits the well established dependence of A on the covalency of the bonds of Mn^{2+} which has four Cl^- as ligands. The measured A is in contrast to the value expected for Mn^{2+} at a Na^+ site with three Cl^- ions and three H_2O molecules as ligands.

From the arguments 1, 3, and 4, we conclude a substitution of Zn^{2+} by Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$.

b) The g-Factor

The mean value $\overline{g} = (g_{\parallel} + g_{\perp})/2 = 2.0019$ of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$, — in case such a value $\overline{g}$ is of any physical meaning —, is equal to the value calculated for pure ionic bonding[5]: $g = 2.0019$. For Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ a bond of mainly ionic character is expected. The mean value $\overline{g}$ as defined above fits well the known scale for g values of Mn^{2+} in different lattices. The remarkable difference between $g_{\parallel}$ and $g_{\perp}$ must be due to a strong crystal field splitting at the Zn^{2+} site of $Na_2ZnCl_4 \cdot 3\,H_2O$.

c) The Hyperfine Splitting Constant A

For Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ the hyperfine splitting constant A is slightly anisotropic. The dominant isotropic part of A amounts to $(-74.4 \pm 0.5) \cdot 10^{-4}$ cm^{-1} and is caused by the Fermi contact interaction between the outer Mn^{2+} electrons and the Mn nucleus.

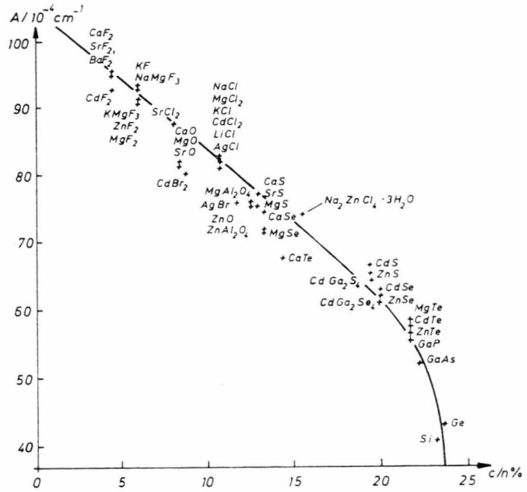

Fig. 4. Dependence of the hyperfine splitting constant A of Mn^{2+} on the covalence of the bond. The values are for the most part taken from Simanek and Müller[7].

As has been shown[6, 7], the isotropic hyperfine constant of Mn^{2+} depends on the covalence of the bond between manganese and its neighbors (Figure 4). Usually the covalence c of a bond between the atoms A and B is calculated by[8]:

$$c = 1 - 0.16\,(X_A - X_B) - 0.035\,(X_A - X_B)^2\,, \qquad (2)$$

where X_A and X_B are the electronegativities[9] of the atoms A and B. To determine the covalence of a bond between the atom A and its n ligands B, c is divided by n.

If we suppose a substitution of Zn^{2+} by Mn^{2+}, the Mn^{2+} ion has four ligands. With[10] $X_{Mn} = 1.4$, and $X_{Cl} = 3.0$, we get $c/n = 16.2\%$. The measured hyperfine constant of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ fits the $A = A(c/n)$ dependence as shown in Figure 4. The anisotropic part of the hyperfine splitting constant of Mn^{2+} is due to a dipole-dipole interaction between the electron spin and the nuclear spin. For S-state ions no dipole-dipole interaction within the Mn^{2+} ion is expected. The fact that an anisotropic part in A is found for Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ indicates a perturbation of the 3d-Mn^{2+} orbitals, due to a strong electric field.

d) The Axial Crystal Field Splitting Constant D

To explain the axial field splitting constant D, a number of models for the interactions between the ground state and the excited states are discussed in the literature. A review of the problem is given by Sharma, Das and Orbach[11–13]. Wybourne[14] and Van Heuvelen[15] showed that the use of relativistic eigenfunctions for the ions might be essential in discussing the crystal field interactions. By semi-empirical methods, a D-value of $-90 \cdot 10^{-4}\,cm^{-1}$ for Mn^{2+} in ionic crystals was calculated[15]. Disagreement between theory and experiment was found for D-values of crystals with a substantial amount of covalent bonding. In $CdGa_2Se_4$, D (Mn^{2+}) is $-919.3 \cdot 10^{-4}\,cm^{-1}$ and this high value is explained by covalent admixtures of the Mn^{2+}-3d functions with the ligand functions[3]. Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$, less covalent bonded than in $CdGa_2Se_4$, shows nearly the same D value in both substances. From this we conclude that the D value of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ must be due dominantly to a very large electric crystal field. The argument of Van Heuvelen that D values much larger in amount than $|-90 \cdot 10^{-4}\,cm^{-1}|$ are due to covalent admixtures cannot be applied to Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$.

As has been shown above, Mn^{2+} substitutes Zn^{2+} and is surrounded by a Cl^- tetrahedron. The X-ray data reveal unequal distances within the $[ZnCl_4]^{2-}$ tetrahedron: Zn-Cl_I = 2.32 Å, Zn-Cl_{II} = 2.26 Å. If the $[MnCl_4]^{2-}$ tetrahedron is distorted in the same manner as the tetrahedron $[ZnCl_4]^{2-}$, the strong crystal field splitting D in the EPR spectrum of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ is not surprising.

The temperature dependence of the parameters of the Spin Hamiltonian of S state ions has been discussed by several authors[16–22]. Two effects contribute to the temperature dependence of the EPR:

1. By thermal lattice expansion the distances between the atoms in the crystal are changed. Consequently, the electric crystal field changes too.
2. Thermally excited phonons modulate the crystal fields and change the population of the electronic states of the paramagnetic ion.

For Mn^{2+} in $CaCO_3$, the first effect is negligible as shown by Serway[22]. He assumed one vibration along the $A_2{}^0$ crystal field amplitude to be dominant and found

$$D(T) = D_0 + \delta \coth(\hbar\,\omega/2\,k\,T)\,. \tag{3}$$

ω is the frequency of the normal mode parallel $A_2{}^0$, and is assumed to be equal for both the ground state and the excited state of the paramagnetic ion. Neglecting the thermal lattice expansion of $Na_2ZnCl_4 \cdot 3\,H_2O$, Eq. (3) is fitted to the experimental values $D(T)$. Figure 2 shows that the measured temperature dependence of D can be satisfactorily described by Equation (3). The following values for the parameters in Eq. (3) were calculated:

$$\begin{aligned} D_0 &= (-1066 \pm 20) \cdot 10^{-4}\ \mathrm{cm}^{-1}\,, \\ \delta &= (120 \pm 20) \cdot 10^{-4}\ \mathrm{cm}^{-1}\,, \\ \omega/2\,\pi &= (117 \pm 10) \cdot 10^{11}\ \mathrm{sec}^{-1} \\ &\mathrel{\widehat{=}} (390 \pm 30)\ \mathrm{cm}^{-1}\,. \end{aligned}$$

By Raman spectroscopy the phonon spectrum of $Na_2ZnCl_4 \cdot 3\,H_2O$ has been investigated[23]. One of the frequencies found and assigned to $[ZnCl_4]^{2-}$ is around 279 cm^{-1}. This is in fair agreement with the vibrational frequency of Mn^{2+} given above. The difference between the two frequencies 390 cm^{-1} and 279 cm^{-1} might be due to the difference in mass and bonding between $[ZnCl_4]^{2-}$ and $[MnCl_4]^{2-}$. No IR or Raman measurements of the vibrational spectrum of $Na_2ZnCl_4 \cdot 3\,H_2O$ doped with Mn^{2+} are available to check the relevance of the phonon frequency deduced from EPR measurements of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ according to Equation (3).

Conclusion

The EPR spectrum of Mn^{2+} in $Na_2ZnCl_4 \cdot 3\,H_2O$ on a Zn^{2+} site reveals strong electric crystal fields, probably due to the distortion of the tetrahedron of Cl^- ions around the Mn^{2+} site. The bonding of the Mn^{2+} ion to the Cl^- ligands corresponds to a bond with about 16% covalent character. The temperature dependence of the axial crystal field parameter D is explained by a vibrational mode of the $[MnCl_4]^{2-}$ complex. The quadrupole splitting constant found from the "forbidden" transitions in the spectrum will be discussed in a following paper.

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[1] A. Weiss and A. Wüst, Z. Naturforsch. **28 a**, 1919 [1973].

[2] A. Wüst, Dissertation, Darmstadt 1973.

[3] M. Schlaak and A. Weiss, Z. Naturforsch. **27 a**, 1624 [1972].

[4] B. Bleaney and R. S. Rubins, Proc. Phys. Soc. London **77**, 103 [1961].

[5] H. Watanabe, Progr. Theor. Phys. **18**, 405 [1957].

[6] O. Matumura, J. Phys. Soc. Japan **14**, 108 [1959].

[7] E. Simanek and K. A. Müller, J. Phys. Chem. Solids **31**, 1027 [1970].

[8] N. B. Hannay and C. F. Smyth, J. Amer. Chem. Soc. **68**, 171 [1946].

[9] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, New York 1960.

[10] W. Gordy and W. J. O. Thomas, J. Chem. Phys. **24**, 439 [1956].

[11] R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. **149**, 257 [1966].

[12] R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. **155**, 338 [1967].

[13] R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. **171**, 378 [1968].

[14] B. G. Wybourne, J. Chem. Phys. **43**, 4506 [1965].

[15] A. Van Heuvelen, J. Chem. Phys. **46**, 4903 [1967].

[16] W. M. Walsh Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139 A**, 1338 [1965].

[17] E. Simanek and Nai Li Huong, Phys. Rev. Letters **17**, 134 [1966].

[18] R. Rosenthal, L. Yarmus, and R. H. Bartram, Phys. Rev. **153**, 407 [1967].

[19] R. Orbach and E. Simanek, Phys. Rev. **158**, 310 [1967].

[20] K. Zdansky, Phys. Stat. Sol. **28**, 181 [1968].

[21] G. Pfister, W. Dreybrodt, and W. Assmus, Phys. Stat. Sol. **36**, 351 [1969].

[22] R. A. Serway, Phys. Rev. **B 3**, 608 [1971].

[23] G. L. Cessac, R. K. Khanna, E. R. Lippincott, and A. R. Bandy, Spectrochimica Acta **28 A**, 917 [1972].

[24] V. Trunz, Diplomarbeit, Technische Universität Clausthal 1970.