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Spin-Lattice Interaction of a Mn^{++} Ion in MgO

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Spin-lattice coupling constants of a Mn^{++} ion in a cubic environment are calculated on the overlap and covalent model. It is found that only the overlap model can account for the signs of the constants in the case of Mn^{++} in MgO, that is, the Mn-O bond is mainly of ionic character. The spin-lattice relaxation time is expressed in terms of the coupling constants for the one phonon process. Its magnitude is a reasonable one, when the observed values of the coupling constants are used.

§ 1. Introduction

An ideal ionic crystal has been defined as being produced by combining highly electropositive metals with highly electronegative elements, each constituent ion having a closed shell structure and being well separated from each other.1)*) The inadequacy of this idealized model of ionic crystals is in the following three respects (see I): (1) overlap; (2) deformation; (3) covalency. Alkali halides are regarded as approximately ideal ionic crystals, and the effects of the three inadequacies have most extensively been investigated on the nuclear quadrupolar relaxation in these crystals (see I). It was found that the overlap effect dominates in crystals with light elements, such as NaCl. Oxides of transition metals have also been investigated along these lines with respect to the superexchange interaction,2) and it was found that the deformation of oxygen ions has the largest contribution to the superexchange interaction in MnO.

Now a Mn^{++} ion, which has a ^6S term, shows a magnetic anisotropy when introduced into a crystal. This occurs because the electrons of the ion is no more spherically symmetrically distributed when it is in a crystal. The deviation from spherical symmetry may come from the above three origins. Watanabe3) considered the deformation of the ion in a crystalline electric field, while the present author4)**) have taken account of the other two effects. When a Mn^{++} ion is introduced into a zinc flouride crystal, in which it is surrounded by six flourine ions, it was found from the sign of the anisotropy constant that the effect of overlap dominates over that of covalency. The magnitude of the overlap integral to account for the observed anisotropy seems to be reasonable. These

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*) This paper will be referred to as I in the following.

**) This paper will be referred to as II in the following.

facts may come from a large electronegativity of a flourine ion and give support to approximate ionic character of the Mn-F bond. Now it is quite interesting to see which effect dominates in a Mn-O bond. Recent measurements$^{5),6)}$ on the spin-lattice interaction constants of a Mn^{++} ion in MgO have revealed this point and its account will be given in the next section. In the third section the spin-lattice relaxation time is expressed in terms of the spin-lattice interaction constants and compared with an experiment.

§ 2. Spin-lattice interaction coefficients

We consider a Mn^{++} ion in a cubic crystal, especially in MgO. A spin Hamiltonian, which is quadratic in spin operators, is generally expressed by

$$H=\sum\nolimits_{i,j=x,y,z} S_i\, D_{ij}\, S_j \tag{1}$$

with $D_{ij}=D_{ji}$ and $D_{xx}+D_{yy}+D_{zz}=0$, x, y, z referring to the crystallographic axes. When the crystal is unstrained, (1) vanishes identically. When it is strained, D's are connected with the strain components by

$$\begin{pmatrix} D_{xx} \\ D_{yy} \\ D_{zz} \\ D_{yz} \\ D_{zx} \\ D_{xy} \end{pmatrix} = \left(\begin{array}{ccc:ccc} G_{11} & -G_{11}/2 & -G_{11}/2 & & & \\ -G_{11}/2 & G_{11} & -G_{11}/2 & & 0 & \\ -G_{11}/2 & -G_{11}/2 & G_{11} & & & \\ \hdashline & & & G_{44} & & 0 \\ & 0 & & & G_{44} & \\ & & & 0 & & G_{44} \end{array}\right) \begin{pmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{pmatrix}, \tag{2}$$

where $e_{xx}=\partial u/\partial x$, $e_{yy}=\partial v/\partial y$, $e_{zz}=\partial w/\partial z$,

$$e_{yz}=\partial v/\partial z+\partial w/\partial y,\quad e_{zx}=\partial w/\partial x+\partial u/\partial z,\quad e_{xy}=\partial u/\partial y+\partial v/\partial x. \tag{3}$$

$\boldsymbol{u}(\boldsymbol{r})=(u(\boldsymbol{r}),\ v(\boldsymbol{r}),\ w(\boldsymbol{r}))$ is the displacement at the position $\boldsymbol{r}$. G_{11} and G_{44} are the spin-lattice coupling coefficients. Using (2) in (1), we have

$$\begin{aligned} H= &(G_{11}/2)\{e_{xx}(3S_x^2-S(S+1))+e_{yy}(3S_y^2-S(S+1))+e_{zz}(3S_z^2-S(S+1))\} \\ &+G_{44}\{e_{yz}(S_yS_z+S_zS_y)+e_{zx}(S_zS_x+S_xS_z)+e_{xy}(S_xS_y+S_yS_x)\}. \end{aligned} \tag{4}$$

Now let us consider the Mn^{++} ion and the six oxygen ions surrounding it (Fig. 1). As shown in the figure, we assume that two ions on the z-axis lie at a distance a' from the Mn^{++} ion, whereas the remaining four ions are at a distance a. The latter are displaced in the x-y plane so that the lines joining them and the center make an angle θ with the x- or y-axis. We have obtained in II the spin Hamiltonian in this situation which is given by

$$H=DS_z^2+E(S_xS_y+S_yS_x), \tag{5}$$

where

$$D=-(9/35)\Delta\cdot P, \tag{6}$$

$$E=(9/35)\,\mu(a)\sin 2\theta\cdot P.^{*)} \tag{7}$$

P was defined in II as

$$P=g^2\mu_B^2(R_0-8R_2/7)+7\langle\xi\rangle^2/3\langle\Delta E\rangle, \tag{8}$$

where R_0 and R_2 are integrals involving r_{12}^{-3}, $\langle\xi\rangle$ a spin-orbit coupling parameter and $\langle\Delta E\rangle$ an average excitation energy from ^{6}S to higher terms. μ was defined by

$$\mu=S^2-\lambda^2, \tag{9}$$

S and λ being the overlap integral and the degree of covalency between the manganous ion and the oxygen ion, respectively (see II). We assume that μ is a function of the distance between them only. Then Δ is defined by

$$\Delta=\mu(a')-\mu(a). \tag{10}$$

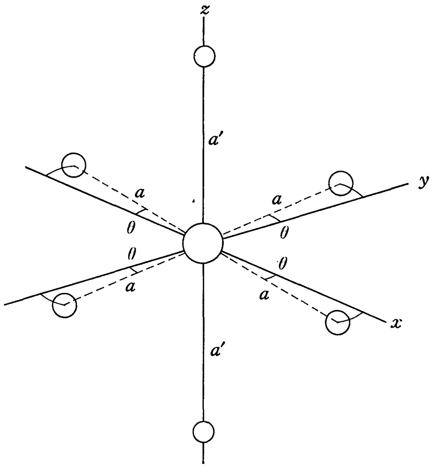

Fig. 1.

It may be reasonable to assume that μ is an exponentially decreasing function of r:

$$\mu(r)=\mu(a)\exp[-\alpha(r-a)/a], \tag{11}$$

where α is a measure of the rapidness of the decrease.

If we consider only linear terms of strains, we have

$$\Delta=-\alpha\mu(a)e_{zz} \tag{12}$$

and

$$\sin 2\theta=-e_{xy}. \tag{13}$$

Using (12) and (13) in (5) with (6) and (7), we have

$$H=(9/35)\,\alpha\mu(a)Pe_{zz}S_z^2-(9/35)\,\mu(a)Pe_{xy}(S_xS_y+S_yS_x). \tag{14}$$

Comparing this expression with (4), we obtain the following expressions for G's:

$$G_{11}=(6/35)\,\alpha\mu(a)P, \tag{15}$$

$$G_{44}=-(9/35)\,\mu(a)P. \tag{16}$$

Recently Watkins and Feher[5)] and Shiren[6)] have measured the amplitude and sign and the amplitude and relative sign, respectively, of G's for the iron-group ions in MgO. Their results are consistent with each other. Since the sign of G is important, we take Watkins' results, which are $G_{11}=+1.3$ and

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*) D and E given here are twice those of (30) and (31) in II. This is because in II only a half of the oxygen ions have been assumed to be displaced from their regular positions.

$G_{44}=-0.27\ \mathrm{cm}^{-1}$/unit strain. Using these in (15) and (16), we have

$$\alpha=7.2, \tag{17}$$

$$\mu(a)P=+1\ \mathrm{cm}^{-1}. \tag{18}$$

From (17) we see that the dependence of μ on r is rather great. That G_{11} is much larger than G_{44} is connected with this fact. From $\alpha=7.2$ we have $\mu\propto \exp(-r/0.29)$, when r is measured in Å, which seems to be reasonable. From (18) we must have $S^2>\lambda^2$, which again indicates that the effect of overlap dominates over the covalency. Blume and Orbach[7] have also calculated G's, considering the deformation of the ion by mixing higher terms under the crystalline electric field which is produced by strains. The calculation seems to be essentially the same as that due to Watanabe. The result is that the signs of G's are in disagreement with the observation. Thus we see that only the overlap effect can account for the signs of the spin-lattice interaction coefficients for a Mn^{++} ion surrounded by oxygen ions.

That the overlap and the covalency appear with the opposite sign in the fine-structure constants, D and E, can be seen as follows: When an oxygen ion is displaced from the regular position towards the Mn^{++} ion, such d orbit that has maximum overlap with the oxygen ion appears with a coefficient greater than unity, i.e. $1+S^2$, in the expression for the charge density of the ion. Then the spin direction for the lowest energy is such that the demagnetizing field is smallest, that is, it is in the direction to the oxygen ion. When covalency is concerned, the d orbit accepts an electron transferred from the oxygen ion, the probability of the electron on the d orbit being λ^2. But the spin direction of this electron is opposite to that of the Mn^{++} ion. The demagnetizing field is the largest in the direction of the oxygen ion, which is then the direction of the maximum energy.

From (18), taking $P=40\ \mathrm{cm}^{-1}$ as in II and neglecting λ^2, we have $S^2=0.025$, which also seems to be a reasonable magnitude.

§ 3. Spin-lattice relaxation time

In this section we shall give a brief account of the calculation of the spin-lattice relaxation time, regarding (4) as a perturbation. We assume that the lattice vibrations are not affected by replacement of a magnesium ion by a manganous ion and restrict ourselves to the one-phonon process. A similar calculation has been done by Blume and Orbach,[7] but we wish to express the relaxation time in terms of the spin-lattice coupling constants, G's. Note that the following result applies not only to the Mn^{++} case but also to any spin in a cubic environment, in which the spin has negligible cubic splitting. The spin must have $S>1/2$, since the interaction (4) is of quadrupole-type, in which case the Van Vleck cancellation does not occur.

First the displacement $\boldsymbol{u}(\boldsymbol{r})$ is analysed in terms of the normal coordinates q_{ks}:

$$\boldsymbol{u}(\boldsymbol{r}) = \sum_{ks} q_{ks} \xi_s(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}), \tag{19}$$

where ξ_s are the unit vectors in the directions of polarization of the mode s, which we assume are orthogonal to each other. q_{ks} has the following matrix elements:

$$\langle N_{ks}-1|q_{ks}|N_{ks}\rangle = \langle N_{ks}|q_{ks}|N_{ks}-1\rangle = (\hbar N_{ks}/2MN\omega_{ks})^{1/2}, \tag{20}$$

where MN is the total mass of the crystal. We assume that the phonon frequency ω_{ks} is independent of s and is given by

$$\omega_{ks} = v_0 k. \tag{21}$$

The direction cosines of the external field H are denoted by l, m, n and p is defined by

$$p = l^2m^2 + m^2n^2 + n^2l^2. \tag{22}$$

Let M denote a component of the spin in the direction of the field. Then the transition probability per unit time from M to $M+1$, for example, is expressed by

$$W(M\to M+1) = (2\pi/\hbar)\sum_{ks}|\langle M\ N_{ks}|H|M+1\ N_{ks}-1\rangle|^2\delta(g\mu_B H - \hbar v_0 k). \tag{23}$$

Using (4), (3), (19), (20) and (21) in (23), we can easily calculate (23). The results for (23) and for other transition probabilities are expressed by

$$W(M\to M\pm 1) = \left\{\frac{3}{4}G_{11}^2 + \left(\frac{4}{3}G_{44}^2 - \frac{3}{4}G_{11}^2\right)p\right\}\frac{(g\mu_B H)^3}{2\pi\rho\hbar^4 v_0^5} \times\left(N_1 + \frac{1}{2} \mp \frac{1}{2}\right)\alpha\left(M - \frac{1}{2} \pm \frac{1}{2}\right), \tag{24}$$

$$W(M\to M\pm 2) = \left\{\frac{3}{4}G_{11}^2 + 4G_{44}^2 - \left(\frac{4}{3}G_{44}^2 - \frac{3}{4}G_{11}^2\right)p\right\} \times\frac{(2g\mu_B H)^3}{2\pi\rho\hbar^4 v_0^5}\left(N_2 + \frac{1}{2} \mp \frac{1}{2}\right)\beta(M-1\pm 1), \tag{25}$$

where ρ is the density of the crystal and

$$N_1 = 1/\{\exp(g\mu_B H/kT) - 1\}, \tag{26}$$

$$N_2 = 1/\{\exp(2g\mu_B H/kT) - 1\}, \tag{27}$$

$$\alpha(M) = (M + \frac{1}{2})^2 (S-M)(S+M+1), \tag{28}$$

$$\beta(M) = (1/16)(S-M-1)(S+M+2)(S-M)(S+M+1). \tag{29}$$

The relaxation time is differently defined according to the conditions of experiments. Here we shall consider the variation with time of the magnetization defined by

$$\langle M\rangle = \sum_M M n_M, \tag{30}$$

when initially the population n_M of each level M is equal so that $\langle M\rangle = 0$. Its variation is expressed by a sum of several exponential functions:

$$\langle M\rangle = \sum_i A_i (1 - \exp(-t/\tau_i)). \tag{31}$$

As has been seen in I, however, (31) can practically be represented by a single exponential function

$$\langle M\rangle = \langle M\rangle_0 (1 - \exp(-t/T_1)), \tag{32}$$

$1/T_1$ being given by comparing the linear terms in t of both expressions. $\langle M\rangle_0$ is the thermal equilibrium value of $\langle M\rangle$.

The rate of change of n_M is given by

$$\begin{aligned} \dot{n}_M = {} & W(M-1\to M)\,n_{M-1} - W(M\to M-1)\,n_M \\ & \qquad + W(M+1\to M)\,n_{M+1} - W(M\to M+1)\,n_M \\ & + W(M-2\to M)\,n_{M-2} - W(M\to M-2)\,n_M \\ & \qquad + W(M+2\to M)\,n_{M+2} - W(M\to M+2)\,n_M. \end{aligned} \tag{33}$$

For small t we put

$$n_M = \{N_0/(2S+1)\}\,(1-\gamma_M t), \tag{34}$$

where γ_M is determined from (33) as

$$\begin{aligned} \gamma_M = {} & W(M\to M-1) - W(M-1\to M) + W(M\to M+1) - W(M+1\to M) \\ & + W(M\to M-2) - W(M-2\to M) + W(M\to M+2) - W(M+2\to M). \end{aligned} \tag{35}$$

Then, for small t, we have from (34)

$$\langle M\rangle = \{N_0/(2S+1)\}\,(\textstyle\sum_M M\gamma_M)\,t. \tag{36}$$

Comparing (36) with (32), we obtain

$$1/T_1 = \{N_0/(2S+1)\}\,(\textstyle\sum_M M\gamma_M)/\langle M\rangle_0. \tag{37}$$

Using (35), (24) and (25) in (37) and noting that

$$\langle M\rangle_0 = N_0 S B_S (g\mu_B SH/kT), \tag{38}$$

we have the following expression for the spin-lattice relaxation time T_1:

$$\frac{1}{T_1} = \frac{3(2S+3)(2S-1)(g\mu_B H)^2 kT}{10\pi\rho\hbar^4 v_0^5}\left\{G_{11}^2 + 2G_{44}^2 + \left(\frac{4}{3}G_{44}^2 - \frac{3}{4}G_{11}^2\right)p\right\}, \tag{39}$$

where we have assumed that $kT \gg g\mu_B H$. When this condition is not satisfied,

kT should be replaced by $(S+1)g\mu_B H/3B_S(g\mu_B SH/kT)$. That $1/T_1$ is proportional to H^2T has been shown by Blume and Orbach.⁷⁾ From (39), we see that T_1 depends on the direction of the applied field. This is peculiar to the one-phonon process. If G_{44} is neglected, it is the longest when H is in [111], where it is 4/3 of that when H is in [100].

When H is measured in koe, v_0 in 10^5 cm/sec, ρ in gr/cm³ and G's in cm⁻¹, (39) becomes

$$1/T_1 = 3.62(2S-1)(2S+3)(g^2H^2T/\rho v_0^5)$$

$$\times\left\{G_{11}^2+2G_{44}^2+\left(\frac{4}{3}G_{44}^2-\frac{3}{4}G_{11}^2\right)p\right\}\ \mathrm{sec}^{-1}. \qquad (40)$$

Blume and Orbach⁷⁾ reported that Castle and Feldman found that $T_1T=1.3$ at X-band. The condition of their experiment is not clear. However, we want to see if (40) gives a correct order of magnitude of the relaxation time. Taking $H=2$, $\rho=3.7$, $v_0=5$, $G_{11}=1.3$, $G_{44}=-0.27$, $S=5/2$ and $p=1/5$, we have $T_1T=3.8$. Thus the agreement may be fairly good.

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