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Spin-Lattice Relaxation of S-State Ions: Mn^{2+} in a Cubic Environment

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The theory of spin-lattice relaxation is developed for S-state ions: in particular for Mn^{2+} in a cubic environment. The wavefunctions for Mn^{2+} are generated to first order in the spin-orbit coupling parameter, the orbit-lattice interaction is formulated in terms of spherical harmonics, and the rate equations are derived for this system. Estimates are given of the interaction coefficients based on a point-charge model, and it is shown that excellent agreement is obtained with observed spin-lattice relaxation times. However, a detailed comparison with recent experiments which give the magnitude and sign of these coefficients directly shows that though the point-charge model gives the right order of magnitude, it gives the wrong sign for the interaction coefficients.

I. INTRODUCTION

THE theory of spin-lattice relaxation in iron-group salts as developed by Waller,[1] Kronig,[2] and Van Vleck[3] has been moderately successful in predicting the order of magnitude and temperature variation of the relaxation times of iron-group ions whose free-ion group states have nonzero orbital angular momentum. According to this theory, a spin in a magnetic field can change its direction (and hence its energy) by absorbing or emitting phonons. This exchange of energy proceeds via the so-called orbit-lattice interaction, a modulation by phonons of the electric crystalline field due to ions surrounding the paramagnetic ion. This field then interacts with the orbital moment of the ion, which in turn interacts with the spin via the spin-orbit coupling, causing transitions between different spin states.

In an S-state ion, such as Mn^{2+}, the orbital angular momentum is zero, and working within a given configuration it is necessary to mix excited states with nonzero angular momentum into the ground state using the spin-orbit coupling to find nonzero matrix elements of the orbit-lattice interaction. This situation is at first sight not very different from that of the non-S-state ions in the iron series. In these ions the orbital angular momentum is usually quenched by the crystalline field and nonzero matrix elements of the orbit-lattice interaction are obtained only after mixing in of excited states via spin-orbit coupling. The excited states in this case may have the same total spin as the ground state, and there will be matrix elements of the orbit-lattice interaction between the ground state and the admixed excited state. Since the admixture is proportional to ζ/Δ, where Δ is the energy of the excited state relative to the ground state and ζ is the spin-orbit coupling constant, the matrix element itself will be proportional to ζ/Δ. In an S-state ion, however, the spin-orbit coupling will mix only states with different total spin values into the ground state. This implies that the matrix elements of the orbit-lattice interaction, which is independent of spin coordinates, will be of order $(\zeta/\Delta)^2$. This is a very small number, and indicates relaxation times longer for Mn^{2+} by 10^2 than for other iron-group salts at low temperatures, other things being equal.

We have calculated the relaxation times for Mn^{2+} in a cubic environment in the low-temperature region, where the direct process (energy exchange by absorption or emission of a single phonon) is expected to be dominant. In the next section we outline briefly the computation of the wave functions for Mn^{2+}. Section III deals with the orbit-lattice interaction and Sec. IV with the resulting rate equations. In Sec. V, we give estimates of the relaxation time based on a point-charge model for the crystalline field, using the results of Van Vleck,[3] and in Sec. VI we compare these estimates with the values recently determined from static strain[4] and microwave saturation measurements.[5]

II. THE WAVEFUNCTIONS FOR Mn^{2+} IN A CUBIC ENVIRONMENT

In Fig. 1 we show the low-lying states of Mn^{2+} in the absence of spin-orbit coupling. On the left are the free-ion sextet and quartet states, while on the right are the states in the presence of a cubic crystalline field. There are three three-fold orbitally degenerate ${}^4\Gamma_4$ states, each of which is a linear combination of the ${}^4G$, ${}^4P$, and ${}^4F$ states. We show only the ${}^4\Gamma_4$ states because the spin-orbit coupling $\zeta\sum_i \mathbf{l}_i\cdot\mathbf{s}_i$ will, to first order, mix into the ${}^6\Gamma_1$ ground state only those states which

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[1] I. Waller, Z. Physik **79**, 370 (1932).

[2] R. de L. Kronig, Physica **6**, 33 (1939).

[3] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939); Phys. Rev. **59**, 730 (1941).

[4] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).

[5] N. S. Shiren, Bull. Am. Phys. Soc. **7**, 29 (1962).

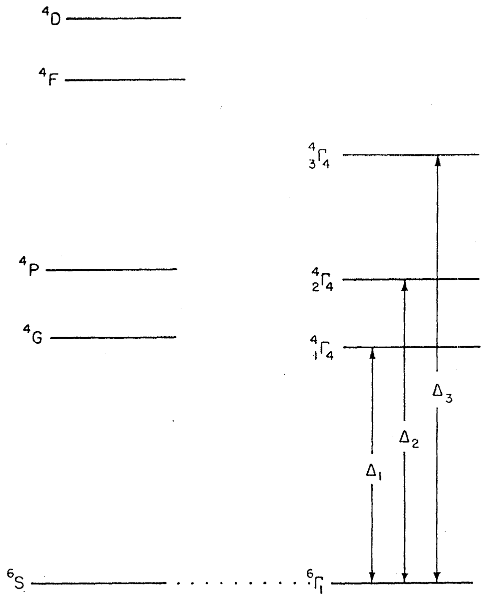

FIG. 1. The low-lying atomic energy levels of Mn^{2+} in the absence of spin-orbit coupling. On the left are indicated the free-ion sextet and quartet states, while on the right are those states suitably admixed in the presence of a cubic crystalline field. The admixture parameters, defined in the text, are given in Table I.

contain ^4P. Using the notation

$$|{}_i^4\Gamma_4\rangle=\alpha_i|^4P\rangle+\beta_i|^4F\rangle+\gamma_i|^4G\rangle, \tag{1}$$

Table I shows the states ${}_i^4\Gamma_4$ and their energies Δ_i relative to the ground state for various values of the cubic field parameter $10Dq$. These values were computed by Powell[6] by direct diagonalization of the cubic field matrix elements.

TABLE I. The cubic field wavefunctions and splittings for various values of Dq. The spin-orbit admixture coefficients of the excited cubic field states into the ground state are also listed. The notation is defined in the text.

i	α_i	β_i	γ_i	Δ_i (cm^{-1})
		$10Dq=9000$ cm^{-1}		
1	0.594	−0.140	0.792	17 256
2	0.784	0.325	−0.530	33 441
3	0.183	−0.935	−0.303	41 303
		$10Dq=10\,000$ cm^{-1}		
1	0.601	−0.148	0.785	16 311
2	0.767	0.383	−0.514	34 000
3	0.225	−0.912	−0.344	41 688
		$10Dq=11\,000$ cm^{-1}		
1	0.607	−0.156	0.779	15 360
2	0.748	0.442	−0.494	34 498
3	0.268	−0.883	−0.385	42 142

M_s	5/2	3/2	1/2	−1/2	−3/2	−5/2
$a(M_s)$	$-\sqrt{5}$	$-\sqrt{3}$	$-\frac{1}{2}\sqrt{6}$	$-\frac{1}{2}\sqrt{2}$	0	0
$b(M_s)$	0	0	$-\frac{1}{2}\sqrt{2}$	$-\frac{1}{2}\sqrt{6}$	$-\sqrt{3}$	$-\sqrt{5}$
$c(M_s)$	0	$-\sqrt{2}$	$-\sqrt{3}$	$-\sqrt{3}$	$-\sqrt{2}$	0

In the absence of spin-orbit coupling, a magnetic field would split the ground state into six states, $|^6SM_s\rangle$ with $M_s=\pm5/2$, $\pm3/2$, and $\pm1/2$. The spin-orbit coupling mixes in the $^4\Gamma_4$ states with the above, and to first order in ζ the wavefunctions are

$$|M_s\rangle=|^6SM_s\rangle-\sum_{ijM_s'}\frac{\langle{}_i^4\Gamma_4jM_s'|\zeta\sum_u \mathbf{l}_u\cdot\mathbf{s}_u|^6SM_s\rangle}{\Delta_i}|{}_i^4\Gamma_4jM_s'\rangle, \tag{2}$$

where the subscript i distinguishes the three different $^4\Gamma_4$ states which occur, and $j=\pm1$, 0 labels the three orbitally degenerate states belonging to each of the ${}_i^4\Gamma_4$. The matrix elements of spin-orbit coupling appearing in (2) were calculated using Racah's[7] coefficients of fractional parentage.

The resulting eigenfunctions can be written as

$$|M_s\rangle=|^6SM_s\rangle-\sum_i\frac{\alpha_i\zeta}{\Delta_i}\{a(M_s)|{}_i^4\Gamma_41M_s-1\rangle+b(M_s)|{}_i^4\Gamma_4-1M_s+1\rangle+c(M_s)|{}_i^4\Gamma_40M_s\rangle\}, \tag{2'}$$

where

$$|{}_i^4\Gamma_41M_s\rangle=\{\alpha_i|P1\rangle+\beta_i[(\tfrac{3}{8})^{\frac{1}{2}}|F1\rangle+(\tfrac{5}{8})^{\frac{1}{2}}|F-3\rangle]+\gamma_i[(\tfrac{7}{8})^{\frac{1}{2}}|G1\rangle+(\tfrac{1}{8})^{\frac{1}{2}}|G-3\rangle]\}|\tfrac{3}{2}M_s\rangle,$$

$$|{}_i^4\Gamma_40M_s\rangle=\{\alpha_i|P0\rangle-\beta_i|F0\rangle+\gamma_i[-(\tfrac{1}{2})^{\frac{1}{2}}|G4\rangle+(\tfrac{1}{2})^{\frac{1}{2}}|G-4\rangle]\}|\tfrac{3}{2}M_s\rangle,$$

$$|{}_i^4\Gamma_4-1M_s\rangle=\{\alpha_i|P-1\rangle+\beta_i[(\tfrac{5}{8})^{\frac{1}{2}}|F3\rangle+(\tfrac{3}{8})^{\frac{1}{2}}|F-1\rangle]+\gamma_i[-(\tfrac{1}{8})^{\frac{1}{2}}|G3\rangle-(\tfrac{7}{8})^{\frac{1}{2}}|G-1\rangle]\}|\tfrac{3}{2}M_s\rangle,$$

and

$$a(M_s)=\tfrac{1}{2}\langle^4P1M_s-1|\textstyle\sum_i l_i^+s_i^-|^6SM_s\rangle,$$
$$b(M_s)=\tfrac{1}{2}\langle^4P-1M_s+1|\textstyle\sum_i l_i^-s_i^+|^6SM_s\rangle,$$
$$c(M_s)=\langle^4P0M_s|\textstyle\sum_i l_i^zs_i^z|^6SM_s\rangle.$$

These coefficients are also shown in Table I.

It is between these states $|M_s\rangle$ that transitions are observed in a paramagnetic resonance or relaxation experiment, and we wish now to calculate the probability per unit time that the orbit-lattice interaction induces a transition between two such levels. The transition probability is related to the relaxation times by the rate equations (see Sec. IV).

One further comment concerning these wavefunctions can be made. It is well known that the ^6S state of the free Mn^{2+} ion splits into a doublet and a quartet state

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[6] M. J. D. Powell (private communication).

[7] G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1943).

on entering a cubic field, with a splitting of about 5×10^{-3} cm^{-1}. This splitting has recently been investigated in detail by Gabriel, Powell, and Johnston,[8] who show that it requires the spin-orbit coupling to fourth order. The magnitude of the splitting is much smaller than those caused by magnetic fields of the size with which we are concerned, and we shall accordingly neglect it in the following.

III. THE ORBIT-LATTICE (OL) INTERACTION

Van Vleck[3] has pointed out that for an octahedron of charges surrounding a paramagnetic ion cluster, vibrations of the type Γ_{3g} and Γ_{5g} are the only terms which need be considered for inducing relaxation transitions. This can be seen by decomposing the motion of the six charges into irreducible representations of the octahedral group O_h (see, Landau and Lifshitz[9]) after subtracting simple translations and rotations of the cluster as a whole. Only even vibrations need be considered as we restrict our matrix elements to be internal to the d^5 configuration. We shall assume the Mn^{2+} ion to be at the center of such a cluster in what follows. It turns out to be suitable for our purposes to express the Γ_{3g} and Γ_{5g} vibrations in terms of Racah's $C_{\lambda\mu}$, writing

$$C_{\lambda\mu}=\sum_i \left[4\pi/(2\lambda+1)\right]^{\frac{1}{2}}Y_\lambda{}^\mu(i).$$

The $Y_\lambda{}^\mu$ are spherical harmonics of orbital index λ and azimuthal quantum number μ.

We, thus, may write

$$\begin{aligned}V_{\mathrm{OL}}&=\sum_{i,j} V_j(\Gamma_{ig})\epsilon(\Gamma_{ig}j)\\&=\sum_{i,j,\lambda,\mu} a_{\lambda\mu}{}^{ij}\langle r^\lambda\rangle C_{\lambda\mu}\epsilon(\Gamma_{ig}j)\\&=\sum_{i,j,\lambda,\mu} V_{\lambda\mu}{}^{ij}C_{\lambda\mu}\epsilon(\Gamma_{ig}j),\end{aligned}\tag{3}$$

where the $\epsilon(\Gamma_{ig}j)$ are those linear combinations of components of the strain tensor which transform as the jth subvector of the representation Γ_{ig}, and the $V_j(\Gamma_{ig})$ are constants. We then group the $C_{\lambda\mu}$ terms in V_{OL}, using the coefficients $a_{\lambda\mu}{}^{ij}$, to transform as Γ_{3g} and Γ_{5g}. We refer to these grouped terms as $V_{\mathrm{OL}}(\Gamma_{3g})$, etc.

We now wish to compute the matrix elements of the $C_{\lambda\mu}$ between the Mn^{2+} wave functions listed in Table I. These matrix elements can also be calculated using the fractional parentage expansion for the d^5 wavefunctions. We find, noting that $C_{\lambda\mu}$ is independent of spin,

$$\langle l^n\alpha'SL'M_sM_L'|C_{\lambda\mu}|l^n\alpha SLM_sM_L\rangle=(-)^{L'-M_L'}\begin{pmatrix}L' & \lambda & L\\ -M_L' & \mu & M_L\end{pmatrix}\langle l^n\alpha'SL'\|C_\lambda\|l^n\alpha SL\rangle,$$

with

$$\begin{aligned}\langle l^n\alpha'SL'\|C_\lambda\|l^n\alpha SL\rangle&=n(2l+1)\left[(2L+1)(2L'+1)\right]^{\frac{1}{2}}\begin{pmatrix}l & \lambda & l\\ 0 & 0 & 0\end{pmatrix}\\&\quad\times\sum_{\alpha_1S_1L_1}(-)^{L+L_1}\langle l^n\alpha'SL'\{|l^{n-1}\alpha_1S_1L_1\rangle\langle l^{n-1}\alpha_1S_1L_1|\}l^n\alpha SL\rangle\begin{Bmatrix}L & \lambda & L'\\ l & L_1 & l\end{Bmatrix},\end{aligned}\tag{4}$$

where the three- and six-j symbols are tabulated by Rotenberg *et al.*,[10] and the fractional percentage coefficients are given by Racah.[7] If we work within the d^5 configuration, only $\lambda\leq4$ gives nonvanishing matrix elements. A simple decomposition of the $C_{\lambda\mu}$'s according to the irreducible representations of the cubic group also limits λ to be even for Γ_{3g} and Γ_{5g}. Hence, we need only consider $\lambda=2, 4$. The linear combinations of $C_{2\mu}$ and $C_{4\mu}$ appropriate to Γ_{3g} and Γ_{5g} are given by Griffith[11]: For $\lambda=2$,

$$\begin{aligned}C_{20}&=C(\Gamma_{3g}2,\theta),\\(C_{22}+C_{2-2})/\sqrt{2}&=C(\Gamma_{3g}2,e);\\C_{2-1}&=C(\Gamma_{5g}2,1),\\(C_{22}-C_{2-2})/\sqrt{2}&=C(\Gamma_{5g}2,0),\\-C_{21}&=C(\Gamma_{5g}2,-1);\end{aligned}\tag{5}$$

and for $\lambda=4$,

$$\begin{aligned}-\frac{\sqrt{5}}{2\sqrt{3}}C_{40}+\frac{\sqrt{7}}{2\sqrt{6}}C_{44}+\frac{\sqrt{7}}{2\sqrt{6}}C_{4-4}&=C(\Gamma_{3g}4,\theta),\\(C_{42}+C_{4-2})/\sqrt{2}&=C(\Gamma_{3g}4,e);\\(\sqrt{7}C_{43}-C_{4-1})/2\sqrt{2}&=C(\Gamma_{5g},4,1),\\(C_{42}-C_{4-2})/\sqrt{2}&=C(\Gamma_{5g}4,0),\\\left[C_{41}-\sqrt{7}C_{4-3})/2\sqrt{2}\right.&=C(\Gamma_{5g}4,-1).\end{aligned}\tag{6}$$

We note that we can now regroup the terms in our expansion for V_{OL}, Eq. (3), into the form

$$\begin{aligned}V_{\mathrm{OL}}=&\sum_{l=2,4}\sum_{m=\theta,\epsilon}V(\Gamma_{3g}l)C(\Gamma_{3g}l,m)\epsilon(\Gamma_{3g},m)\\&+\sum_{l=2,4}\sum_{m=\pm1,0}V(\Gamma_{5g}l)C(\Gamma_{5g}l,m)\epsilon(\Gamma_{5g},-m)(-1)^m;\end{aligned}\tag{7}$$

where[11]

$$\begin{aligned}\epsilon(\Gamma_{3g},\theta)&=\tfrac{1}{2}(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy}),\\\epsilon(\Gamma_{3g},\epsilon)&=\tfrac{1}{2}\sqrt{3}(\epsilon_{xx}-\epsilon_{yy}),\\\epsilon(\Gamma_{5g},1)&=-i(3/2)^{\frac{1}{2}}(\epsilon_{yz}+i\epsilon_{zx}),\\\epsilon(\Gamma_{5g},0)&=i\sqrt{3}\epsilon_{xy},\\\epsilon(\Gamma_{5g},-1)&=i(3/2)^{\frac{1}{2}}(\epsilon_{yz}-i\epsilon_{zx}),\end{aligned}\tag{8}$$

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[8] J. R. Gabriel, M. J. D. Powell, and D. F. Johnston, Proc. Roy. Soc. (London) **A264**, 503 (1961).

[9] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, New York, 1958), p. 367.

[10] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (Technology Press, Massachusetts Institute of Technology, Cambridge, 1959).

[11] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, New York, 1961).

so that there are only four phenomenological coefficients we need to evaluate from experiment. In fact this number reduces to three, as $C(\Gamma_{3g}2,m)$ accidentally does not contribute to the relaxation transitions for Mn^{2+} in a cubic environment.

If we substitute these expressions into (4) and compute the required matrix elements between the admixed states of Table I, we find the only nonvanishing matrix elements to be

$$\begin{aligned}
&\langle M_s=\tfrac{5}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=\tfrac{3}{2}\rangle=\{-(5/7)\surd 6(\zeta^2\textstyle\sum)V(\Gamma_{5g}2)+(4\surd 10)((1/21)\zeta^2\sum+(1/12)\zeta^2\sum')V(\Gamma_{5g}4)\}\epsilon(\Gamma_{5g}1);\\
&\langle M_s=\tfrac{5}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=\tfrac{1}{2}\rangle=\{[5(\surd 6)/14](\zeta^2\textstyle\sum)V(\Gamma_{5g}2)-(2\surd 10)((1/21)\zeta^2\sum+(1/12)\zeta^2\sum')V(\Gamma_{5g}4)\}\epsilon(\Gamma_{5g}0);\\
&\langle M_s=\tfrac{5}{2}|V_{\mathrm{OL}}(\Gamma_{3g})|M_s=\tfrac{1}{2}\rangle=\tfrac{1}{3}\surd 5(\zeta^2\textstyle\sum-2\zeta^2\sum')V(\Gamma_{3g}4)\epsilon(\Gamma_{3g}e);\\
&\langle M_s=\tfrac{3}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=\tfrac{1}{2}\rangle=\{-(2/7)(\surd 15)(\zeta^2\textstyle\sum)V(\Gamma_{5g}2)+8((1/21)\zeta^2\sum+(1/12)\zeta^2\sum')V(\Gamma_{5g}4)\}\epsilon(\Gamma_{5g}1);\\
&\langle M_s=\tfrac{3}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=-\tfrac{1}{2}\rangle=\{[3(\surd 30)/14]\zeta^2\textstyle\sum\ V(\Gamma_{5g}2)-(\sqrt{2}/2)((4/7)\zeta^2\sum+\zeta^2\sum')V(\Gamma_{5g}4)\}\epsilon(\Gamma_{5g}0);\\
&\langle M_s=\tfrac{3}{2}|V_{\mathrm{OL}}(\Gamma_{3g})|M_s=-\tfrac{1}{2}\rangle=\tfrac{1}{2}\sqrt{2}(\zeta^2\textstyle\sum-2\zeta^2\sum')V(\Gamma_{3g}4)\epsilon(\Gamma_{3g}e);
\end{aligned}\tag{9}$$

where the transitions are labeled by the dominant part of the state vector, and the two symbols $\sum$ and $\sum'$ are defined by

$$\begin{aligned}\textstyle\sum&=\textstyle\sum_{jj'}\alpha_j\alpha_j'\beta_j\gamma_j'/\Delta_j\Delta_j';\\ \textstyle\sum'&=\textstyle\sum_{jj'}\alpha_j\alpha_j'\alpha_j\gamma_j'/\Delta_j\Delta_j';\end{aligned}\tag{10}$$

the α, β, and γ's being defined as in Table I. For a reasonable choice of the Racah parameters, $B=800$ cm^{-1}, $C=3200$ cm^{-1}, we find for $10Dq=10^4$ cm^{-1},

$$\begin{aligned}\textstyle\sum&=-0.268\times10^{-10}\ \mathrm{cm}^2;\\ \textstyle\sum'&=6.292\times10^{-10}\ \mathrm{cm}^2.\end{aligned}$$

Using a value for ζ of 300 cm^{-1}, we, thus, find

$$\begin{aligned}
&\langle M_s=\tfrac{5}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=\tfrac{3}{2}\rangle\\
&\qquad=\{0.422V(\Gamma_{5g}2)+5.09V(\Gamma_{5g}4)\}\\
&\qquad\qquad\times\epsilon(\Gamma_{5g}1)\times10^{-5};\\
&\langle M_s=\tfrac{5}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=\tfrac{1}{2}\rangle\\
&\qquad=\{-0.211V(\Gamma_{5g}2)-2.911V(\Gamma_{5g}4)\}\\
&\qquad\qquad\times\epsilon(\Gamma_{5g}0)\times10^{-5},\\
&\langle M_s=\tfrac{5}{2}|V_{\mathrm{OL}}(\Gamma_{3g})|M_s=\tfrac{1}{2}\rangle\\
&\qquad=-6.095V(\Gamma_{3g}4)\epsilon(\Gamma_{3g}e)\times10^{-5};\\
&\langle M_s=\tfrac{3}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=\tfrac{1}{2}\rangle\\
&\qquad=\{0.267V(\Gamma_{5g}2)+3.22V(\Gamma_{5g}4)\}\\
&\qquad\qquad\times\epsilon(\Gamma_{5g}1)\times10^{-5};\\
&\langle M_s=\tfrac{3}{2}|V_{\mathrm{OL}}(\Gamma_{5g})|M_s=-\tfrac{1}{2}\rangle\\
&\qquad=\{-0.283V(\Gamma_{5g}2)-3.906V(\Gamma_{5g}4)\}\\
&\qquad\qquad\times\epsilon(\Gamma_{5g}0)\times10^{-5},\\
&\langle M_s=\tfrac{3}{2}|V_{\mathrm{OL}}(\Gamma_{3g})|M_s=-\tfrac{1}{2}\rangle\\
&\qquad=-8.177V(\Gamma_{3g}4)\epsilon(\Gamma_{3g}e)\times10^{-5}.
\end{aligned}\tag{11}$$

These are the phenomenological expressions for the matrix elements of V_{OL} with which we shall work.

IV. THE RATE EQUATIONS FOR THE DIRECT PROCESS

The matrix elements of V_{OL} have now been computed in terms of the three phenomenological coefficients $V(\Gamma_{3g}4)$, $V(\Gamma_{5g}2)$, and $V(\Gamma_{5g}4)$. It is now a simple matter to set up the rate equations for the populations of the sublevels of the ground term of the Mn^{2+} ion. The procedure has recently been outlined by Andrew and Tunstall,[12] and, thus, we shall not go into detail here. If we define the deviation of the population of a given level from thermal equilibrium as n_{M_s}, and then use the differences $N_{2M_s-1}=\frac{1}{2}(n_{M_s}+n_{M_s-1})$ and assume our system is prepared symmetrically so that $N_{2M_s-1}=N_{1-2M_s}$, we find

$$\begin{aligned}
\dot N_2&=-N_2[2A_{5/2\to3/2}+A_{5/2\to1/2}]\\
&\qquad+N_1[A_{3/2\to1/2}+A_{3/2\to-1/2}-A_{5/2\to1/2}]\\
&\qquad\qquad+N_0[A_{3/2\to-1/2}],\\
\dot N_1&=N_2[A_{5/2\to3/2}-A_{5/2\to1/2}]\\
&\qquad-N_1[2A_{3/2\to1/2}+A_{5/2\to1/2}],\\
\dot N_0&=N_2[2A_{5/2\to1/2}]+N_1[2A_{5/2\to1/2}+A_{3/2\to1/2}]\\
&\qquad-N_0[2A_{3/2\to1/2}],
\end{aligned}\tag{12}$$

where the $A_{M_s\to M_s'}$ are the transition probabilities per unit time to go between the levels M_s and M_s'. It is a difficult matter to compute these terms for a real crystal, as the phonon spectrum must be known for an arbitrary crystal direction. What we shall do in order to estimate T_1 is to assume the host crystal is isotropic, and neglect the directional properties of the linear combinations of the strain tensors appropriate to our dynamic crystalline field coefficients $V(\Gamma_{ig}l)$. We do make use, however, of the orthogonality of the linear combinations of the strain to eliminate cross terms when we go on to square our perturbation matrix element.

It is now a simple matter to compute the $A_{M_s\to M_s'}$.[13] We find, for $g\beta H\ll kT$,

$$A_{M_s\to M_s'}=\frac{3g^2\beta^2H^2kT}{\pi h^4\rho v^5}\times\sum_{m,i}\Big|\sum_{l}\langle M_s'|C(\Gamma_{ig},lm)|M_s\rangle V(\Gamma_{ig}l)\Big|^2.\tag{13}$$

It is now obvious that $A_{M_s\to M_s'}\neq0$ only for $|M_s-M_s'|\leq2$, as V_{OL} can only connect states differing in M_s by ≤2. This follows because we have used the spin-orbit

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[12] E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. (London) **78**, 1 (1961).

[13] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

coupling only once in determining the admixed eigenfunctions $|M_s\rangle$. We now return to our rate equations and solve them for some special cases. Consider the case when the same spin temperature exists for all levels and $N_0=N_1=N_2$. This is the usual condition for nonresonant relaxation time measurements, and gives rise to the relaxation time

$$1/T_1=(4/35)(A_{5/2\to3/2}+4A_{5/2\to1/2}+4A_{3/2\to-1/2}+A_{3/2\to1/2}). \quad (14)$$

In the case of more general initial conditions, and the application of microwave pulse techniques, the situation is more complex. In general, all adjacent levels do not have the same relative population and a spin temperature does not necessarily exist for the system as a whole. In such cases we must return to the rate equations and include the initial conditions explicitly. There will be three relaxation times and any *given* population difference, N_2, N_1, or N_0, will not decay in a simple exponential fashion, but as a linear combination of three exponentials. We can compute these times by assuming $N_{2M_s-1}\propto e^{-\lambda t}$. Thus, we have from (12), the secular equation,

$$\begin{vmatrix} \lambda-(2A_{5/2\to3/2}+A_{5/2\to1/2}) & A_{3/2\to1/2}+A_{3/2\to-1/2}-A_{5/2\to1/2} & A_{3/2\to-1/2} \\ A_{5/2\to3/2}-A_{5/2\to1/2} & \lambda-(2A_{3/2\to1/2}+A_{5/2\to1/2}) & 0 \\ 2A_{5/2\to1/2} & 2A_{5/2\to1/2}+2A_{3/2\to1/2}-2A_{3/2\to-1/2} & \lambda-2A_{3/2\to-1/2} \end{vmatrix}=0. \quad (15)$$

The three eigenvalues represent the three values for the relaxation time, and the eigenvector for a given eigenvalue represents the linear combination of population differences which decay according to the single exponential with a relaxation time equal to the inverse of the eigenvalue. It is a simple matter to use a linear combination of the three eigenvectors which satisfies $t=0$ conditions and to note how a given population will decay in time.

V. ESTIMATION OF THE COUPLING COEFFICIENTS ON A POINT-CHARGE MODEL

In his original work on this subject, Van Vleck expressed the orbit-lattice interaction in the form $V_{\mathrm{OL}}=\sum_i V_iQ_i$, $i=2,\cdots,6$, where the Q_i are the even modes of vibration for the surrounding octahedron of ligands. By expanding the Q_i in terms of the normal modes of vibration of the entire crystal (phonons), Van Vleck obtained an expression for V_{OL} which is equivalent to our Eq. (3). This decomposition in effect expresses the Q_i in terms of $R\epsilon$, where R is the anion-cation distance ($=2.10$Å$=3.97a_0$ for MgO) and ϵ is one of the strain components.

The V_i in Van Vleck's expression for V_{OL} were given by him in terms of the Cartesian coordinates of the electrons rather than in a spherical-harmonic expansion as in Eq. (13). He gives:

$$\begin{aligned} V_2&=\sum\{A(x_0^2-y_0^2)+B(x_0^4-y_0^4)\}, \\ V_3&=\sum\{A(x_0^2+y_0^2-2z_0^2)+(B/\sqrt{3})(x_0^4+y_0^4-2z_0^4)\}, \\ V_4&=\sum\{Cx_0y_0+E(x_0^3y_0+x_0y_0^3)\}, \\ V_5&=\sum\{Cx_0z_0+E(x_0^3z_0+x_0z_0^3)\}, \\ V_6&=\sum\{Cy_0z_0+E(y_0^3z_0+z_0^3y_0)\}, \end{aligned} \quad (16)$$

where x_0, y_0, z_0 are the Cartesian coordinates of the electrons of the paramagnetic ion relative to the position of their nucleus and A, B, C, E are constants. These constants are related to our $V(\Gamma_{ig}l)$ in (3); $V(\Gamma_{3g}2)$ and $V(\Gamma_{3g}4)$ are linear combinations of A and B, and $V(\Gamma_{5g}2)$ and $V(\Gamma_{5g}4)$ are linear combinations of C and E. In order to make a crude estimate of the $V(\Gamma_{ig}l)$, we adopt Van Vleck's point-charge model for the crystalline field, representing the surrounding O^{--} ions by point charges ee_{eff}. Van Vleck finds, on this model,

$$\begin{aligned} A&=\tfrac{1}{4}ee_{\mathrm{eff}}(18R^{-4}-75R^{-6}r_0^2); \\ B&=(175/8)ee_{\mathrm{eff}}R^{-6}; \\ C&=ee_{\mathrm{eff}}(-6R^{-4}+15R^{-6}r_0^2); \\ E&=(-35/2)ee_{\mathrm{eff}}R^{-6}. \end{aligned} \quad (17)$$

Comparing (16) and (17) with (3), and taking account of all normalization factors, we find

$$\begin{aligned} V(\Gamma_{3g}2)&=6ee_{\mathrm{eff}}\langle r^2\rangle/R^3, \\ V(\Gamma_{3g}4)&=-(5/3)(15)^{\frac{1}{2}}ee_{\mathrm{eff}}\langle r^4\rangle/R^5, \\ V(\Gamma_{5g}2)&=4ee_{\mathrm{eff}}\langle r^2\rangle/R^3, \\ V(\Gamma_{5g}4)&=-\tfrac{2}{3}(15)^{\frac{1}{2}}ee_{\mathrm{eff}}\langle r^4\rangle/R^5. \end{aligned} \quad (18)$$

Noting that $ee_{\mathrm{eff}}<0$, we have $V(\Gamma_{3g}2)$ and $V(\Gamma_{5g}2)<0$ and $V(\Gamma_{3g}4)$ and $V(\Gamma_{5g}4)>0$.

We are now left with the task of estimating the several parameters in these expressions. Taking the observed value of R for MgO, we need only two other quantities, which we take to be $ee_{\mathrm{eff}}\langle r^4\rangle$ and the ratio $\langle r^2\rangle/\langle r^4\rangle$. The first quantity can be estimated by using Penney and Schlapp's point-charge expression[14] for $10Dq$, the static cubic field splitting:

$$10Dq=-(5/3)ee_{\mathrm{eff}}\langle r^4\rangle R^{-5}. \quad (19)$$

Setting this equal to the probable experimental value[8] of 10 000 cm^{-1}, we find

$$ee_{\mathrm{eff}}\langle r^4\rangle=-26.96a_0^4. \quad (20)$$

An approximate value for $\langle r^2\rangle/\langle r^4\rangle$ can be obtained by using values for these quantities obtained from free-ion Hartree-Fock wavefunctions. Unpublished calculations

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[14] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); R. Schlapp and W. G. Penney, *ibid.* **42**, 666 (1932).

of Freeman and Watson give

	Mn^{2+}	Mn^{+}
$\langle r^2\rangle$	$1.548a_0^2$	$2.026a_0^2$
$\langle r^4\rangle$	$5.513a_0^4$	$10.872a_0^4$
$\langle r^2\rangle/\langle r^4\rangle$	$0.280a_0^{-2}$	$0.186a_0^{-2}$

(21)

The Mn^+ values are shown since use of these may partially compensate for the expansion of the wavefunctions upon going from the free ion to the solid.[15] Using $\langle r^2\rangle/\langle r^4\rangle\approx 0.2a_0^{-2}$, we find

$$\begin{aligned} V(\Gamma_{3g}2)&=-11.3\times10^4\ \mathrm{cm}^{-1},\\ V(\Gamma_{3g}4)&=3.85\times10^4\ \mathrm{cm}^{-1},\\ V(\Gamma_{5g}2)&=-5.32\times10^4\ \mathrm{cm}^{-1},\\ V(\Gamma_{5g}4)&=1.08\times10^4\ \mathrm{cm}^{-1}. \end{aligned} \tag{22}$$

This procedure is, of course, extremely rough and we expect only an order of magnitude estimate from it. The $V(\Gamma_{ig},l)$ depend sensitively on the lattice parameter R, and we have assumed that this quantity remains unchanged on substitution of Mn for Mg. The uncertainty in this procedure is at least as great as that used in estimating the ratio $\langle r^2\rangle/\langle r^4\rangle$. Covalency effects are expected to play an important role in the determination of these coefficients, and since even the static parameter $10Dq$ has not been calculated accurately,[16] we cannot hope for more than order-of-magnitude agreement with experiment for the $V(\Gamma_{ig}l)$, which are associated with *distortions* of the octahedral complex.

With the values of $V(\Gamma_{ig}l)$ given by (22), we can proceed to compute T_1 as given by (14). Using $\rho=3.7$ g/cm^3, $v=5\times10^5$ cm/sec, we find

$$1/T_1=0.134H^2T\ \mathrm{sec}^{-1}, \tag{23}$$

where H is measured in kilogauss and T in degrees Kelvin. At X band, this implies a T_1T product of 1.8 sec deg, which is of the same order of magnitude as the value 1.6 sec deg recently found by Castle and Feldman.[17]

VI. COMPARISON OF THE ORBIT-LATTICE COEFFICIENTS WITH RECENT DIRECT EXPERIMENTAL MEASUREMENTS

Recently, Watkins and Feher[4] and Shiren[5] have succeeded in measuring the amplitude and sign and the amplitude and relative sign, respectively, of the orbit-lattice interaction coefficients for the iron-group ions in MgO. In particular, they have measured these coefficients for Mn^{2+} in this host crystal. Our three parameters $V(\Gamma_{3g}4)$, $V(\Gamma_{5g}2)$, and $V(\Gamma_{5g}4)$ can be combined into only two independent coefficients, as a glance at Eq. (9) will show, since certain linear combinations of them always occur together. These coefficients are designated by the above authors as G_{11} and G_{44}. They describe the orbit-lattice interaction in a spin-Hamiltonian notation as $\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}$. The $\mathbf{D}$ tensor is related to the strain by $\mathbf{D}=\mathbf{G}\boldsymbol{\varepsilon}$, or in the Voigt notation $D_j=\sum_k G_{jk}\epsilon_k$ $(j,k=1, 2, \cdots, 6)$. In a cubic material, only two coefficients are independent, $G_{11}(=-2G_{12})$ and G_{44}. The measured values are:

	Watkins and Feher[4]	Shiren[5]
G_{11}	$+1.3$ cm^{-1}/unit strain	±1.4 cm^{-1}/unit strain
G_{44}	-0.27 cm^{-1}/unit strain	∓0.28 cm^{-1}/unit strain

(24)

It is straightforward to re-express our coefficients in terms of the G's. We find

$$\begin{aligned} G_{11}&=\frac{\sqrt{6}}{9}\{\zeta^2\textstyle\sum-2\zeta^2\sum'\}V(\Gamma_{3g}4);\\ G_{44}&=-\left(\frac{3\sqrt{10}}{52}\zeta^2\textstyle\sum\right)V(\Gamma_{5g}2)\\ &\qquad+\frac{\sqrt{6}}{2}\left[\frac{\zeta^2}{21}\textstyle\sum+\frac{\zeta^2}{12}\sum'\right]V(\Gamma_{5g}4). \end{aligned} \tag{25}$$

Using the point-charge results for the $V(\Gamma_{ig},l)$ and our previous estimates of ζ, $\sum$, and $\sum'$, we find

$$\begin{aligned} G_{11}&=-1.21\ \mathrm{cm}^{-1}/\text{unit strain};\\ G_{44}&=0.0782\ \mathrm{cm}^{-1}/\text{unit strain}. \end{aligned} \tag{26}$$

The point-charge model appears to give the wrong sign for these coefficients, and somewhat smaller magnitudes as well. There is a cancellation in the expression for G_{44} which is sensitive to the $\langle r^4\rangle/\langle r^2\rangle$ ratio, but not in the expression for G_{11}. The agreement of our computed T_1 with experiment occurs because the relaxation time depends only on the magnitude and not on the sign of these coefficients.

VII. CONCLUSIONS

The orbit-lattice interaction appears to account adequately for the relaxation times of S-state ions, in spite of the relatively long times found experimentally for these substances. The point-charge model gives values of the same order of magnitude but of opposite sign to the experimental orbit-lattice parameters, indicating that it cannot be taken too seriously in this type of theory.

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[15] Suggestion by Dr. A. J. Freeman.

[16] A. Freeman and R. Watson, Phys. Rev., **120**, 1254 (1960); R. G. Shulman and S. Sugano, Phys. Rev. Letters, **7**, 157 (1961).

[17] J. G. Castle and D. W. Feldman (to be published).