

the other should overlap the low-field resonance. Some traces of this may be detected in our charts when H lies close to $[011]$, but, if it is there, its components are very weak. We have no explanation of this at the present time.

The values $\gamma=0.69$, $\delta^2=1.05$ lie close to what is expected by interpolation of Lea, Leask, and Wolf's points to $x=-0.55$. This may be compared⁵ with $x=0.6$ for Dy^{3+} ; $-0.6 < x < -0.4$ for Dy^{++} ; $x=-0.7$ for Nd^{3+} from optical measurements; $x \sim -0.46$ for Ho^{++} (and probably Er^{3+} also) and $x=0.74$ for Tm^{++} . In all these cases the contributions from fourth- and sixth-

order terms are comparable. Contrast Vincow and Low's conclusion that $x=-1.0$ (no sixth-order contribution) for Nd^{3+} . Our value for x in the isoelectronic Pr^{++} , on the other hand, follows the same general trend as other divalent and trivalent ions in calcium fluoride. This result sheds further doubt on Vincow and Low's conclusions.

As will be seen from Figs. 1 and 2, the hyperfine structure of Pr^{++} is anisotropic and, in view of the anisotropy already present owing to the Γ_8 quartet structure, difficult to analyze quantitatively. It is hoped to report on this further in a future communication.

Temperature Dependence of Hyperfine Coupling of S-State Ions in Cubic Environment*

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The experiments of Walsh, Jeener, and Bloembergen on $\text{Mn}^{2+}:\text{MgO}$ exhibit a hyperfine-coupling constant A which decreases with increasing temperature, contrary to the contribution from lattice thermal expansion. This paper proposes a mechanism in which excited s -like configurations are admixed into the $3d^5$ configuration by the orbit-lattice interaction. The hyperfine field resulting from such admixtures is opposite to the $T=0$ (primarily core polarization) hyperfine field. As the amplitude of phonon vibrations is thermally increased, a net decrease of A is predicted, the temperature dependence of which is in agreement with the results of Walsh *et al.* An estimate of the magnitude of this mechanism using a near-neighbor point-charge model falls somewhat short of the observed magnitude, but the discrepancy is shown to originate in the evaluation of the orbit-lattice coupling constant. In view of the primitive model currently used to compute these coupling constants, agreement in magnitude of the calculated and observed shift is as good as can be expected.

I. INTRODUCTION

RECENTLY Walsh, Jeener, and Bloembergen¹ have studied the temperature dependence of the hyperfine coupling of Mn^{2+} and V^{2+} ions in various cubic crystals. A particularly interesting result of their study is the observation of a decrease of the hyperfine-coupling constant A with increasing temperature, whereas hydrostatic-pressure experiments² predict an increase of A with temperature in $\text{Mn}^{2+}:\text{MgO}$ and $\text{Mn}^{2+}:\text{ZnS}$ (caused by thermal expansion of the lattice). There is thus evidence of an appreciable explicit temperature dependence of the hyperfine-coupling constant A for Mn^{2+} in these crystals.

We should like to propose a mechanism which may be responsible for this effect. The mechanism involves the admixture of excited configurations of the form

$3d^4ns$ into the ground $3d^5$ configuration by a dynamic phonon-induced noncubic field. Since this dynamic field is electrostatic in character, the admixed s states will have spin parallel to the spin of the $3d^5$ ground state. This will result in a net decrease of hyperfine field since the hyperfine coupling in the ground $3d^5$ configuration is produced primarily by core polarization. The latter is known to produce a hyperfine field of negative sign compared to that of an s electron with the same spin direction.³ Because we use phonons to induce the s -like admixtures, the net change in hyperfine field will be proportional to the mean-square strain $\langle \epsilon^2 \rangle$, a quantity which increases as the fourth power of the temperature (or as the total heat) at low temperatures.

In order to estimate this effect quantitatively, we shall adopt a perturbation approach for the computation of strain-induced s admixtures. It is now well known that this will provide only a very rough estimate,⁴ but it will prove possible at the end of the computation to replace the admixture coefficients with

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¹ W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. 139, A1338 (1965).

² W. M. Walsh, Jr., Phys. Rev. 122, 762 (1961).

³ V. Heine, Phys. Rev. 107, 1002 (1957).

⁴ T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956).

a more accurate nonperturbation (in the usual sense) expression using the results of Sharma *et al.*⁵ This expression arises from a numerical integration of the Schrödinger equation containing both the free-ion and axial-field potential, a method originally proposed by Sternheimer.⁶ This method of calculation will yield a result dependent on the strength of the axial potential. If a near-neighbor point-charge model appropriate to MgO is adopted, it is shown in Sec. IV that while the *temperature* dependence of the hyperfine-coupling constant $A(T)$ is predicted correctly, the experimental magnitude of the strength of the variation is an order of magnitude larger than that which we find theoretically. A similar discrepancy was also found in the work of Blume and Orbach⁷ who attempted to compute the strain splitting of the ground 6S multiplet of Mn^{2+} in MgO. If we scale up their results so as to obtain the correct strain splitting (an increase of roughly a factor of 3), and then use the new coefficients in our calculation, agreement is found with the magnitude of the hyperfine shift as well as its temperature dependence. This may be a valid procedure since in both computations only the near neighbors were assumed to contribute to the $l=2$ axial-field terms. It is known that these coefficients receive contributions from ions far away from the local cluster, so that a proper point-charge summation might well substantially increase the $l=2$ orbit-lattice coefficients.

In the next section, the perturbed one-electron orbitals are obtained in the presence of phonon-induced noncubic crystalline fields. In Sec. III the average change in hyperfine field caused by these perturbed orbitals is computed, and in Sec. IV a discussion of the results is given.

II. THE PERTURBED ONE-ELECTRON ORBITALS

We shall take as our starting point a $3d^5$, 6S paramagnetic ion (e.g., Mn^{2+}) at the center of an octahedral arrangement of oppositely charged ions. The presence of a phonon excitation in the crystal will produce an electrostatic crystalline-field potential of axial or rhombic symmetry at the site of the paramagnetic ion. This potential is usually referred to as the orbit-lattice interaction and has the form⁷

$$V_{OL} = \sum_{m=\theta, \epsilon} V(\Gamma_{3g}, 2) C(\Gamma_{3g}, 2, m) \epsilon(\Gamma_{3g}, m) + \sum_{m=\pm 1, 0} V(\Gamma_{5g}, 2) C(\Gamma_{5g}, 2, m) \epsilon(\Gamma_{5g}, -m) (-1)^m. \quad (1)$$

Only $l=2$ terms are kept since we need only consider $d \rightarrow s$ admixtures. The $\epsilon(\Gamma_{ig}, m)$ are linear combinations

of components of the strain tensor transforming as the m th subvector of the Γ_{ig} irreducible representation of the cubic group. They are given by

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

The functions $C(\Gamma_{ig}, 2, m)$ are linear combinations of spherical harmonics Y_2^m of the form⁷

$$\begin{aligned} C(\Gamma_{3g}, 2, \theta) &= (4\pi/5)^{1/2}(Y_2^0), \\ C(\Gamma_{3g}, 2, \epsilon) &= (4\pi/10)^{1/2}(Y_2^2 + Y_2^{-2}), \\ C(\Gamma_{5g}, 2, 1) &= (4\pi/5)^{1/2}Y_2^{-1}, \\ C(\Gamma_{5g}, 2, 0) &= (4\pi/10)^{1/2}(Y_2^2 - Y_2^{-2}), \\ C(\Gamma_{5g}, 2, -1) &= -(4\pi/5)^{1/2}Y_2^1. \end{aligned} \quad (3)$$

These quantities have transformation properties similar to the $\epsilon(\Gamma_{ig}, m)$ and describe the angular dependence of the dynamic crystal field. The coupling parameters $V(\Gamma_{ig}, 2)$ can be calculated by adopting a point-charge model for the crystal field of the surrounding octahedron of charges. Blume and Orbach,⁷ using such a model, find

$$\begin{aligned} V(\Gamma_{3g}, 2) &= 6ee_{\text{eff}}(r^2/R^3), \\ V(\Gamma_{5g}, 2) &= 4ee_{\text{eff}}(r^2/R^3), \end{aligned} \quad (4)$$

where e is the electronic charge, e_{eff} the effective anion charge, R the anion-cation distance, and r the radial distance of the $3d$ electron from the center of the paramagnetic ion. We shall use this explicit form for $V(\Gamma_{ig}, 2)$ for convenience, but it should be emphasized that our results are more general than is implied by the use of this model.

It is now necessary to use (1) to admix excited s character into the ground $3d$ functions. Conventional perturbation theory would yield

$$\psi_{3d\alpha}' = \psi_{3d\alpha} - \sum_n \frac{\langle \psi_{ns} | V_{OL} | \psi_{3d\alpha} \rangle}{E(3d\alpha) - E(ns)} \psi_{ns}, \quad (5)$$

where α labels the particular $3d$ orbital being considered. In the free Mn^{2+} ion,⁸ $E(3d) - E(4s) = -62\,850 \text{ cm}^{-1}$. The use of this and similar values of $E(ns)$ for other excited ns states neglects the effect of the cubic crystalline field.

It is of interest to examine (5) for the specific case of the $m=0$, (Γ_{3g}, θ) $3d$ orbital because it allows direct comparison with the results of Sharma *et al.*⁵ Consider the first term in (1) for $m=\theta$ and insert it in (5). It is

⁵ R. Orbach, T. P. Das, and R. R. Sharma, in *Proceedings of the International Conference on Magnetism, Nottingham* (The Institute of Physics and The Physical Society, London, 1964), p. 330; R.R. Sharma, T. P. Das, and R. Orbach, *Phys. Rev.* (to be published).

⁶ R. M. Sternheimer and H. Foley, *Phys. Rev.* **102**, 961 (1956).

⁷ M. Blume and R. Orbach, *Phys. Rev.* **127**, 1587 (1962).

⁸ C. E. Moore, *Natl. Bur. Std. (U.S.) Circ. No. 467* (1957), Vol. 2.

not difficult to show that

$$\psi_{3d_0}' = \psi_{3d_0} - \frac{6e\epsilon_{\text{eff}}}{(\sqrt{5})R^3} \sum_n \frac{\langle \psi_{ns} | r^2 | \psi_{3d} \rangle}{E(3d) - E(ns)} \epsilon(\Gamma_{3g}, \theta) \psi_{ns}. \quad (6)$$

Sharma *et al.*⁵ avoid the use of conventional perturbation theory and instead solve the Schrödinger equation numerically using (1) as a perturbing potential. For the same orbit-lattice term and the same $3d_\alpha$ orbital as we consider in (6), Sharma *et al.* find

$$\psi_{3d_0}' = \psi_{3d_0} + \frac{6e\epsilon_{\text{eff}}}{(\sqrt{20\pi})R^3} \frac{\mu_{d \rightarrow s}^{(1)}}{r} \epsilon(\Gamma_{3g}, \theta). \quad (7)$$

This enables us to identify the sum in (6) as

$$-\sum_n \frac{\langle \psi_{ns} | r^2 | \psi_{3d_0} \rangle}{E(3d) - E(ns)} \psi_{ns} = \frac{\mu_{d \rightarrow s}^{(1)}}{(\sqrt{4\pi})r}. \quad (8)$$

We will make use of this result in Sec. IV.

III. COMPUTATION OF THE HYPERFINE FIELD

We now construct the 6S , $M_s = \frac{5}{2}$ component of the $3d^5$ configuration using orbitals perturbed by the orbit-lattice interaction, viz., (5). The ground-state determinant is simply

$$|{}^6S', M_s = \frac{5}{2}\rangle = |\psi_{3d_{4z}}'^+ \psi_{3d_{4x}}'^+ \psi_{3d_0}^+ \psi_{3d_{-1}}'^+ \psi_{3d_{-2}}'^+\rangle, \quad (9)$$

where $\psi_{3d_\alpha}'^+$ is the perturbed $3d_\alpha$ orbital with up spin. The perturbed hyperfine field is found from the matrix element of

$$H_{\text{hyp}} = (8\pi/3)g\mu_\beta \sum_i s_{zi} \delta(\mathbf{r}_i), \quad (10)$$

where \mathbf{r}_i labels the position of the i th electron with spin component s_{zi} . The matrix element of (10) between states (9) is

$$\begin{aligned} \langle {}^6S', M_s | H_{\text{hyp}} | {}^6S', M_s \rangle &= (8\pi/3)g\mu_\beta M_s (e\epsilon_{\text{eff}}/R^3)^2 \\ &\times \sum_n \sum_{n'} \frac{\langle \psi_{3d} | r^2 | \psi_{ns} \rangle \langle \psi_{n's} | r^2 | \psi_{3d} \rangle}{[E(3d) - E(ns)][E(3d) - E(n's)]} \\ &\times \langle \psi_{ns} | \delta(r) | \psi_{n's} \rangle (1/25) \{ 36(\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) \\ &- 36(\epsilon_{zz}\epsilon_{xx} + \epsilon_{xx}\epsilon_{yy} + \epsilon_{zz}\epsilon_{yy}) \\ &+ 48(\epsilon_{yz}^2 + \epsilon_{zx}^2 + \epsilon_{xy}^2) \}. \quad (11) \end{aligned}$$

Though the individual ϵ_{ij} time-average to zero, their square does not, so that a time-averaged value for $\langle H_{\text{hyp}} \rangle$ obtains in (11). The average value of $\langle H_{\text{hyp}} \rangle$ can be found using thermal averages for the squares of the strains appearing in (11). These averages have been computed recently by Orbach and Pincus⁹ using a

⁹ R. Orbach and P. Pincus, Phys. Rev. **143**, 168 (1966).

Debye approximation and Van Vleck's¹⁰ averaging procedure for a cubic crystal. We find, in the same manner, that

$$\begin{aligned} \langle H_{\text{hyp}} \rangle_{\text{av}} &= (8\pi/3)g\mu_\beta S_z (e\epsilon_{\text{eff}}/R^3)^2 \\ &\times \sum_n \sum_{n'} \frac{\langle \psi_{3d} | r^2 | \psi_{ns} \rangle \langle \psi_{n's} | r^2 | \psi_{3d} \rangle}{[E(3d) - E(ns)][E(3d) - E(n's)]} \\ &\times \langle \psi_{ns} | \delta(r) | \psi_{n's} \rangle \frac{18\hbar}{25\rho\pi^2} \left(\frac{1}{v_t^5} + \frac{2}{3v_l^5} \right) \left(\frac{k_B T}{\hbar} \right)^4 \\ &\times \int_0^{\Theta/T} \frac{x^3 dx}{(e^x - 1)}, \quad (12) \end{aligned}$$

where ρ is the mass density of the crystal, v_t and v_l are the transverse and longitudinal sound velocities, respectively, and Θ is the averaged Debye temperature of the crystal. In (12) the temperature-independent zero-point contribution to $\langle \epsilon_{ij}^2 \rangle$ has been omitted. Its magnitude is small compared to the static hyperfine field $H_c = A \langle S_z \rangle / g_N \mu_N$ resulting from core polarization. Using the relation between the total hyperfine field at the nucleus and the hyperfine coupling constant A , (12) implies

$$A(T) = A(T=0) \left(1 - CT^4 \int_0^{\Theta/T} \frac{x^3 dx}{(e^x - 1)} \right), \quad (13)$$

so that we find the departure of A from its $T=0$ value follows the total lattice heat. Using the relation (8), we can find C in (13) by comparing with (12). We have

$$\begin{aligned} C &= \frac{(8\pi/3)g\mu_0 \langle S_z \rangle \lim_{r \rightarrow 0} \mu_{d \rightarrow s}^{(1)} / (\sqrt{4\pi})r^2}{H_c} \\ &\times \frac{18}{25} \left(\frac{e\epsilon_{\text{eff}}}{R^3} \right)^2 \frac{\hbar}{\rho\pi^2} \left(\frac{1}{v_t^5} + \frac{2}{3v_l^5} \right) \left(\frac{k_B}{\hbar} \right)^4. \quad (14) \end{aligned}$$

IV. DISCUSSION OF RESULTS

There are two rather independent aspects of our proposed mechanism which should be compared with the experimental results of Walsh *et al.*¹ The first is the temperature dependence of the shift of the hyperfine-coupling constant $A(T)$ predicted by (13). The integral appearing in (13),

$$I = T^4 \int_0^{\Theta/T} \frac{x^3 dx}{(e^x - 1)}, \quad (15)$$

has been evaluated numerically in the temperature range 0–800°K assuming a Debye temperature $\Theta = 750^\circ\text{K}$. The value of Θ was obtained using the

¹⁰ J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

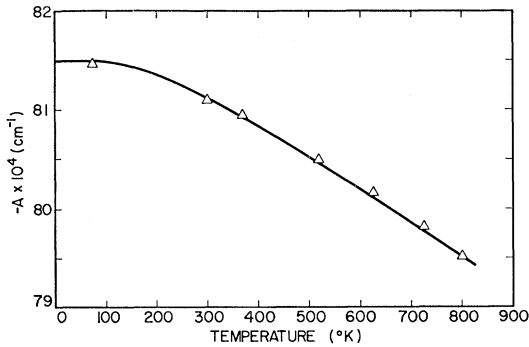


FIG. 1. The theoretical value of the phonon-induced shift of the hyperfine coupling constant A for $\text{Mn}^{2+}:\text{MgO}$, calculated from (13) with $\Theta=750^\circ\text{K}$, is plotted against temperature. The parameter $C=2.58 \times 10^{-13} (\text{°K})^{-4}$ is obtained by fitting the theoretical expression for $A(T)-A(0)$ to the experimental shift at $T=800^\circ\text{K}$. Points designated by Δ are experimental values for $A(T)$, corrected for lattice expansion, from Walsh *et al.* (see Ref. 1).

low-temperature specific-heat data of Giaque and Archibald.¹¹ The parameter C appearing in (13) was evaluated by fitting to the experimental value of $A(T)$ at $T=800^\circ\text{K}$. We find $C_{\text{expt}}=2.58 \times 10^{-13} (\text{°K})^{-4}$. The theoretical expression (13) for $A(T)$ is plotted in Fig. 1 together with the experimental values of Walsh *et al.*¹ after correction for the effect of thermal expansion. It is seen that the predicted temperature dependence of the hyperfine-coupling constant $A(T)$ is in quite remarkable agreement with experiment. The departure of the measured values of $A(T)$ from the predicted temperature dependence (13) is less than the experimental error, $\pm 0.05\%$, in the determination of $A(T)$. In our opinion, the very close agreement exhibited in Fig. 1 demonstrates that dynamic phonon effects are responsible for the observed temperature dependence of the hyperfine-coupling constant $A(T)$. [Note added in proof. A recent private communication from Dr. W. M. Walsh indicates that instead of a T^4 temperature dependence of A in the low-temperature region, as predicted by our Eqs. (12) and (13), he measured a $T^{1.5}$ dependence. We have no explanation for this observed departure from our predicted behavior.]

The second aspect of our calculation is the predicted magnitude of C , the coefficient of the temperature-dependent term in (13). In Secs. II and III we adopted a near-neighbor point-charge model to evaluate the strength of the orbit-lattice coupling. The resulting expression for C is given in (14). Values of the constants appearing therein appropriate to MgO are $\rho=3.7 \text{ g/cm}^3$, $R=2.1 \text{ \AA}$, and $e_{\text{eff}}=-2e$. We use Huntington's¹² values for $v_t=6.3 \times 10^5 \text{ cm/sec}$, $v=8.8 \times 10^5 \text{ cm/sec}$,

Sharma's¹³ value for

$$\left| \lim_{r \rightarrow 0} \frac{\mu_{d \rightarrow s}^{(1)}}{(\sqrt{4\pi})rR^3} \right|^2 = 0.298 \text{ a.u.} \quad (16)$$

$$= 2.02 \times 10^{24} \text{ cm}^{-3},$$

and Walsh's¹ value for $H_c=575 \text{ kG}$. Inserting all of these quantities into (14) we find,

$$C=0.30 \times 10^{-13} (\text{°K})^{-4}, \quad (17)$$

to be compared with

$$C_{\text{expt}}=2.58 \times 10^{-13} (\text{°K})^{-4}, \quad (18)$$

obtained above. As pointed out in the Introduction, the theoretical near-neighbor point-charge estimate of C is about an order of magnitude smaller than the experimental value. This magnitude of discrepancy is rather common in point-charge estimates of the orbit-lattice coupling constant. In fact, Blume and Orbach,⁷ using the same model, find a value of G_{44} (proportional to $V(\Gamma_{5g},2)$ and $V(\Gamma_{5g},4)$) of $\sim \frac{1}{3}$ the experimental value found by Watkins and Feher,¹⁴ Shiren,¹⁵ and Feher.¹⁶ This latter discrepancy may be removed when the overlap contribution originally proposed by Kondo^{17,18} is taken into account properly.⁵ Our results will be unaffected by such corrections because C depends only on s -electron admixtures to the $3d^5$ configuration. Another source of error may lie in the near-neighbor approximation we have used to compute $V(\Gamma_{ig},2)$. The contribution to the $l=2$ terms in the orbit-lattice interaction from more distant ions should be quite significant but as yet no quantitative estimates of these added terms is available. If we assume that the point-charge contribution to $V(\Gamma_{5g},2)$ dominates the overlap contribution, and adjust the Blume-Orbach results to yield a value of G_{44} in agreement with experiment, $V(\Gamma_{5g},2)$ is enhanced by a factor of 3 and our theoretical result for C (proportional to $[V(\Gamma_{3g},2)]^2$) (17) is brought into equality with Walsh's observations.

In conclusion, we have demonstrated that the temperature dependence of the hyperfine-coupling constant of $\text{Mn}^{2+}:\text{MgO}$ matches what would be expected from dynamic phonon contributions. A quantitative numerical estimate of the magnitude of phonon-induced s admixtures to the $3d^5$ configuration seems to fall somewhat short of the observed value, but this may be caused by the naïvete of the near-neighbor point-charge model.

¹³ R. R. Sharma, private communication. We are indebted to Dr. Sharma for making his results available to us prior to publication.

¹⁴ G. D. Watkins and E. Feher, *Bull. Am. Phys. Soc.* **7**, 29 (1962).

¹⁵ N. S. Shiren, *Bull. Am. Phys. Soc.* **7**, 29 (1962).

¹⁶ E. Feher, *Phys. Rev.* **136**, A145 (1964).

¹⁷ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **23**, 106 (1960).

¹⁸ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **28**, 1026 (1962).

¹¹ W. F. Giaque and R. C. Archibald, *J. Am. Chem. Soc.* **59**, 561 (1937).

¹² H. B. Huntington, *Solid State Phys.* **7**, 214 (1958).