

Ref. 1.

¹⁰Note that Eqs. (7) and (10) are valid only to first order in the quantity $\eta \equiv [A^2 M_0^2 \chi_N(T)]/K$. Considering the coupling to (say) the Mn^{55} spin system at low tem-

peratures in a material with an anomalously low magnetic anisotropy such as $RbMnF_3$ one finds that $\eta \approx 1$. The expansion is no longer valid and a more complete solution is required.

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Generalized Theory for the Temperature-Dependent Hyperfine Coupling Constant of Iron-Group S -State Ions*

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The orbit-lattice interaction theory describing the temperature dependence of the hyperfine coupling constant of iron-group S -state ions in cubic crystals is generalized by means of the same k -space averaging method employed in the generalization of the theory for rare-earth S -state ions. This generalized theory provides a good qualitative fit to experimental data on the temperature behavior of the hyperfine constant of Mn^{2+} in CaF_2 , SrF_2 , and BaF_2 , but the calculated magnitude of the decrease in the hyperfine constant with temperature is considerably smaller (with respect to its observed value) than is the corresponding magnitude calculated from the long-wavelength theory. This disagreement between theory and experiment increases with increasing interionic distance in the host lattice. In addition, the generalized theory for iron-group S -state ions confirms our previous finding that optical phonons make a significant contribution to both the thermal and rigid-lattice values of the hyperfine coupling constant, and enables us to determine the range of validity of the long- and short-wavelength treatments.

In an earlier paper,¹ the orbit-lattice interaction theory for the temperature dependence of the hyperfine coupling constant of rare-earth S -state ions in cubic crystals was generalized by employing an expansion technique which enabled us to treat the wavelength of the lattice vibrations exactly over the entire phonon spectrum. By means of this expansion the use of the long- or the short-wavelength approximation was avoided. In this paper, we present the generalized theory for the temperature dependence of the hyperfine coupling constant of iron-group S -state ions in cubic crystals and apply it to the $A(T)$ data on Mn^{2+} in the alkaline earth fluorides.

It is important to note that an isotropic lattice is assumed in our generalized treatment of the k -space averaging, that is, we assume that each phonon branch can be decomposed into one longitudinal and two degenerate transverse modes, whereas this is true in a real lattice only at certain symmetry points in the reduced zone. Nevertheless, this is a common assumption which has been employed in orbit-lattice interaction theory since it was originally introduced,² and without which it would be difficult to proceed.

The expression for the orbit-lattice interaction V_{01} given in Eq. (1) of Ref. 3 can be used as a starting point in formulating the generalized theo-

ry, with the following important exception: There are three modes transforming like Γ_{5g} which vanish in the long-wavelength approximation and therefore could be ignored in Ref. 3, but they must be included in the present generalized treatment. It should also be noted that the equation derived for either the rare-earth or the iron-group ions are applicable to both the XY_6 and XY_8 molecular clusters under the relationship

$$V_{01}(XY_8) = -\frac{8}{9} V_{01}(XY_6). \quad (1)$$

The calculation of the perturbed hyperfine field for iron-group S -state ions proceeds in a manner analogous to the calculation for the rare-earth S -state ions presented in Refs. 1 and 3. The final generalized expression for the temperature-dependent hyperfine constant is⁴

$$A(T) = A(0) \left\{ 1 - D_{ac} F_{ac}(T) - \sum_r^{n-1} [D_{op} F_{op}(T)]_r \right\}, \quad (2)$$

where the summation is taken over all optical branches of the spectrum. The constant D_{ac} is given by

$$D_{ac} = \frac{8\pi}{3} \frac{g\mu_B \langle S_z \rangle}{H_c} \left(\frac{ee'}{R^4} \right) \sum_{n,n'} U_{nn'} \frac{81\hbar}{80\rho\pi^2 v_t^3} \left(\frac{k_B}{\hbar} \right)^2 \quad (3)$$

in units of K^{-2} , and

$$U_{nn'} = \frac{\langle R_{3d} | r^2 | R_{ns} \rangle \langle R_{n's} | r^2 | R_{3d} \rangle}{[E(3d) - E(ns)][E(3d) - E(n's)]} \times \langle \Psi_{ns} | \delta(r) | \Psi_{n's} \rangle, \quad (4)$$

where R_{3d} , R_{ns} are the radial parts of the atomic orbitals. All other symbols have been defined in Ref. 1. The unitless constant D_{op} is given by

$$D_{op} = \frac{8\pi}{3} \frac{g\mu_B \langle S_z \rangle}{H_c} \left(\frac{ee'}{R^5} \right)^2 \sum_{n,n'} U_{nn'} \frac{81\hbar}{80\rho\pi^2} \left(\frac{1}{R\omega_t} \right) = D_{ac} \left(\frac{\hbar}{k_B} \right)^2 \left(\frac{v_t}{R} \right)^3 \frac{1}{\omega_t}. \quad (5)$$

Using a Debye spectrum for the acoustic branch, we obtain

$$F_{ac}(T) = T^2 (I_t + I_t'), \quad (6)$$

$$I_t = \left(\frac{v_t}{v_t'} \right)^3 \int_0^{\Theta'/T} \left(1 - \frac{1}{9} [10j_2(\rho_1^t) - 11j_0(\rho_1^t)] + \frac{1}{45} [32j_2(\rho_2^t) - 55j_0(\rho_2^t)] \right. \quad (7)$$

$$\left. + \frac{1}{5} [4j_2(\rho_3^t) - 5j_0(\rho_3^t)] \right) \frac{x dx}{e^x - 1},$$

$$I_t' = 2 \int_0^{\Theta'/T} \left\{ 1 + \frac{1}{9} [5j_2(\rho_1^t) + 11j_0(\rho_1^t)] - \frac{1}{45} [16j_2(\rho_2^t) + 55j_0(\rho_2^t)] - \frac{1}{5} [2j_2(\rho_3^t) + 5j_0(\rho_3^t)] \right\} \frac{x dx}{e^x - 1}, \quad (8)$$

where

$$\rho_1^\sigma = \left(\frac{8}{3} \right)^{1/2} K^\sigma x, \quad \rho_2^\sigma = \left(\frac{4}{3} \right)^{1/2} K^\sigma x, \quad \rho_3^\sigma = 2K^\sigma x, \quad (9)$$

$$K^\sigma = Rk_B T / v_\sigma \hbar, \quad x = \hbar\omega / k_B T. \quad (10)$$

In addition, we have for the zero-point acoustic phonon contribution,

$$F_{ac}^0 = \frac{D_{ac}}{2} \left(\frac{\Theta'}{z} \right)^2 v_t^3 \left\{ \left(\frac{1}{2v_t^3} + \frac{1}{v_t^3} \right) z^2 - \frac{1}{40} \left(\frac{3}{v_t} + \frac{82}{v_t} \right) - \frac{1}{8} \left(\frac{7}{v_t} \cos z_1^t + \frac{4}{v_t} \cos z_1^t \right) + \frac{5}{4v_t z_1^t} \right. \\ \times \left(\sin z_1^t - \sin z_1^t \right) + \frac{1}{20} \left(\frac{29}{v_t} \cos z_2^t + \frac{26}{v_t} \cos z_2^t \right) \\ \left. - \frac{8}{5v_t z_2^t} \left(\sin z_2^t - \sin z_2^t \right) + \frac{3}{20} \left(\frac{3}{v_t} \cos z_3^t \right) \right\} \quad (11)$$

$$+ \frac{2}{v_t} \cos z_3^t \left. - \frac{3}{5v_t z_3^t} \left(\sin z_3^t - \sin z_3^t \right) \right\}, \quad (11)$$

where

$$z_1^\sigma = \left(\frac{8}{3} \right)^{1/2} z / v_\sigma, \quad z_2^\sigma = \left(\frac{4}{3} \right)^{1/2} z / v_\sigma, \quad z_3^\sigma = 2z / v_\sigma, \quad (12)$$

$$\text{and } z = Rk_B \Theta' / \hbar. \quad (13)$$

An Einstein spectrum yields the following equations for the optical branches:

$$F_{op}(T) = \left\{ \left[\frac{\omega_t / \omega_1}{e^{\hbar\omega_t / k_B T} - 1} + \frac{2}{e^{\hbar\omega_t / k_B T} - 1} \right] L_1 - \left[\frac{\omega_t / \omega_1}{e^{\hbar\omega_t / k_B T} - 1} - \frac{1}{e^{\hbar\omega_t / k_B T} - 1} \right] L_2 \right\}, \quad (14)$$

$$L_1 = \left(\frac{y_D^2}{18} \right) [6y_D + 11\sqrt{\frac{3}{2}} j_1(\sqrt{\frac{8}{3}} y_D) - 11\sqrt{3} j_1(\sqrt{\frac{4}{3}} y_D) - 9j_1(2y_D)], \quad (15)$$

$$L_2 = \frac{2}{45} \int_0^{y_D} [25j_2(\sqrt{\frac{8}{3}} y) - 16j_2(\sqrt{\frac{4}{3}} y) - 18j_2(2y)] y^2 dy. \quad (16)$$

Finally, we have for the zero-point optical phonon contribution

$$F_{op}^0 = \frac{1}{2} D_{op} [(\omega_t / \omega_1 + 2)L_1 - (\omega_t / \omega_1 - 1)L_2]. \quad (17)$$

To recover the long-wavelength limit, we expand the equations for the acoustic branch about $\rho = 0$ and $z = 0$, as shown in Ref. 1. It can be shown that the generalized equations reduce exactly to those obtained by Simanek and Orbach³ in the long-wavelength approximation⁵ for all temperatures T . The range of validity of the long-wavelength approximation is therefore independent of temperature and governed roughly by the condition $k_D R \lesssim \frac{1}{2}$.

The short-wavelength limit is investigated using the expansions presented in Ref. 1. It can be shown that the equations for the acoustic branch become

$$F_{ac}(T) \rightarrow v_t^3 T^2 \int_0^{\Theta'/T} \left\{ \frac{1}{v_t^3} \left[x + \frac{1}{K^t} \left(\frac{1}{6} \sqrt{\frac{3}{2}} \sin \rho_1^t - \frac{87\sqrt{3}}{90} \sin \rho_2^t - \frac{9}{10} \sin \rho_3^t \right) \right] \right. \\ \left. + \frac{2}{v_t^3} \left[x + \frac{1}{K^t} \left(\frac{1}{3} \sqrt{\frac{3}{2}} \sin \rho_1^t - \frac{13\sqrt{3}}{30} \sin \rho_2^t - \frac{3}{10} \sin \rho_3^t \right) \right] \right\} (e^x - 1)^{-1} dx. \quad (18)$$

Equation (18) is not of the same form as the expression derived by Huang⁶ who obtains only the terms linear in χ . The additional terms in Eq. (18) can be neglected when the largest of their coefficients is small with respect to unity. Thus, the range of validity of the short-wavelength approximation is determined by the condition

$$T \gg \frac{7}{6} \sqrt{\frac{3}{2}} (v_1 \hbar / R k_B). \quad (19)$$

This inequality depends only on the parameters of the host crystal. In CaF_2 , for example, the condition (19) yields $T \gg 340 \text{ K}$, which is an impractically high-temperature region.

Comparison between the generalized theory and experimental results will be confined here to the alkaline earth fluorides. Data on $\text{CaF}_2:\text{Mn}^{2+}$ ⁷ and on $\text{SrF}_2:\text{Mn}^{2+}$ ⁸ were obtained by Serway and on $\text{BaF}_2:\text{Mn}^{2+}$ by Huang *et al.*⁹ In all three hosts no data were available below 77 K, and hence the values of $A(0)$ had to be obtained by extrapolation to $T = 0$. Values of the parameters appropriate to the three host crystals are listed in Table III of Ref. 1, and we take $e' = -e$. Hartree-Fock-Slater calculations show that only the excited $4s$ orbitals contribute, so the sum in Eq. (3) is restricted to $n = n' = 4$. The value of U_{44} in Eq. (4) was obtained from the corrected¹⁰ relationship for $\mu_d^{(1)}$ provided by Simanek and Orbach³ for $\text{MgO}:\text{Mn}^{2+}$:

$$\left| \lim_{r \rightarrow 0} \frac{\mu_d^{(1)}}{r} \frac{e^2}{R^3} \right|^2 = 4\pi \left(\frac{e^2}{R^3} \right)^2, \quad U_{44} = 2.02 \times 10^{24} \text{ cm}^{-3}. \quad (20)$$

It can be shown that, within experimental error, both the long-wavelength and the generalized theories fit the functional dependence of A on T equally well. Theoretical values D_{ac}^{theor} of the

constant D_{ac} were calculated from Eq. (3), and the theoretical values of C , denoted by C^{theor} , were evaluated via Eq. (14) of Ref. 3. Their values, along with those of D_{ac}^{expt} and C^{expt} , are recorded in Table I for Mn^{2+} in the three alkaline earth fluorides. Ratios of the experimental to the theoretical values of these coefficients for the two theories are also listed in Table I. The results are similar to those obtained for Eu^{2+} in these same host materials, viz., for all three hosts and for both the approximate and the generalized theories, the theoretical values of the coefficients are smaller than the experimental values, but the disparity is actually greater for the generalized theory. Consequently, it must be concluded that the point-charge lattice-continuum model is, in fact, a poorer description of the behavior of $A(T)$ than was originally thought.

In keeping with our efforts to restrict the generalized theory to a single adjustable parameter (D_{ac}), the ratio of the optical to the acoustic contribution (D_{op}/D_{ac}) was fixed by expression (5), and hence D_{op} was not treated as a free parameter. From Eq. (5) it was found that the optical contribution to $A(T)$ for Mn^{2+} at room temperature was 24% in the CaF_2 crystal, 26% in SrF_2 , and 21% in BaF_2 . These values are consistent with those calculated for Eu^{2+} in the same crystals and demonstrate that optical phonons make a significant contribution to $A(T)$.

The zero-point contribution ΔA_{ZP} to the hyperfine coupling constant and the rigid-lattice value A_{RL} can be calculated in the manner presented in Ref. 1. These quantities were calculated for both the generalized and the long-wavelength theories by using D_{ac}^{expt} and C^{expt} , respectively. Their values are listed in Table II. Again it is found

TABLE I. Experimental and theoretical values of D_{ac} (in K^{-2}) and C (in K^{-4}) for Mn^{2+} in CaF_2 , SrF_2 , and BaF_2 .

Host	$10^7 D_{ac}^{\text{expt}}$	$10^{10} D_{ac}^{\text{theor}}$	$D_{ac}^{\text{expt}}/D_{ac}^{\text{theor}}$	$10^{12} C^{\text{expt}}$	$10^{14} C^{\text{theor}}$	$C^{\text{expt}}/C^{\text{theor}}$
CaF_2	1.22	9.46	129	1.68	5.87	28.6
SrF_2	1.87	6.83	274	4.35	6.32	68.8
BaF_2	3.86	7.19	537	14.4	12.3	117

TABLE II. Values of $A(0)$, ΔA_{ZP} , and A_{RL} (in 10^{-4} cm^{-1}) from the generalized and long-wavelength models for Mn^{2+} in CaF_2 , SrF_2 , and BaF_2 .

Host	Generalized model			Long-wavelength model	
	$A(0)^a$	ΔA_{ZP}	A_{RL}	ΔA_{ZP}	A_{RL}
CaF_2	-95.35	0.969	-96.32	1.33	-96.68
SrF_2	-95.40	0.879	-96.28	1.08	-96.48
BaF_2	-93.60	0.898	-94.50	1.06	-94.66

^a $A(0)$ values in CaF_2 , SrF_2 , and BaF_2 were obtained from Refs. 7, 8, and 9, respectively.

that the behavior of A_{RL} for Mn^{2+} is similar to its behavior for Eu^{2+} , i. e., the rigid-lattice values for the three host crystals are not equal, and A_{RL} in BaF_2 is considerably smaller than its values in CaF_2 and SrF_2 . Furthermore, the optical phonon contributions to ΔA_{ZF} are 46, 51, and 47% for Mn^{2+} in CaF_2 , SrF_2 , and BaF_2 , respectively.

In conclusion, for both rare-earth^{11,12} and iron-group³ S-state ions in cubic crystals, the calculated strength of the coupling constant D_{ac} in the generalized theory is considerably smaller (with respect to its measured value) than is the corresponding value of C in the long-wavelength model. Moreover, the disagreement between theory and experiment increases with increasing lattice constant of the host crystal. It has also been shown that (1) optical phonon branches make a significant

contribution to $A(T)$ and to A_{RL} , and therefore should not be neglected in the calculations; (2) the short-wavelength treatment⁶ has validity only at unrealistically high temperatures; and (3) the validity of the long-wavelength treatment³ is independent of temperature but is restricted to the condition $k_D R \lesssim \frac{1}{2}$.

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⁴Equations (23), (31), and (38) of Ref. 1 are incorrectly written; they should not contain the zero-point contributions.

⁵This is also true for the optical branches, although no long-wavelength treatment of the optical branches

has ever been published.

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