COVALENCY AND TEMPERATURE DEPENDENCE OF HYPERFINE COUPLING Mn^{2+} IN MgO[†]

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A covalent model is suggested for the calculation of the temperature dependence of hyperfine coupling. The results of calculations on Mn^{2+} in MgO show that covalent admixtures of inner shells form an important contribution to the strength of the temperature dependence.

In a previous paper, one of the present authors and Orbach[1] have proposed a mechanism for the explicit temperature dependence of the hyperfine interaction of Mn^{2+} in cubic crystals. A near-neighbor point-charge model has been adopted to evaluate the phonon-induced admixture of the excited $3d^4ns$ states into the ground $3d^5$ configuration of Mn^{2+} in MgO, and it has been shown that the calculated strength of the variation of the hyperfine constant A is an order of magnitude smaller than that deduced from measurements by Walsh, Jeener, and Bloembergen.[2] The purpose of the present note is to show that this discrepancy can be reduced by taking into account covalency effects in calculating the phonon-induced hyperfine field. The importance of covalent delocalization of the d electrons for the temperature dependence has been pointed out by Walsh, Jeener, and Bloembergen, who have observed that the smaller the absolute value of A the greater the temperature dependence. We consider a Mn^{2+} ion in a cubic crystal, especially MgO. The σ antibonding orbitals of the $(MnO_6)^{10-}$ octahedral complex are

$$\psi_u = N(\varphi_u - \lambda_\sigma \chi_u), \quad \text{transforming like } (3z^2 - r^2),$$

$$\psi_v = N(\varphi_v - \lambda_\sigma \chi_v), \quad \text{transforming like } (x^2 - y^2), \tag{1}$$

where φ_u, φ_v are atomic d functions and χ_u, χ_v are linear combinations of $2p_\sigma$ oxygen orbitals.[3] It has been shown recently[4,5] that spin density can be transmitted from p_σ ligand orbitals to central ion s shells by overlap and transfer effects. In a perfect octahedron the overlap integrals of the orbitals ψ_u and ψ_v with the central ion s functions φ_{ns} are zero, but a phonon excitation in the crystal distorts ψ_u and ψ_v so that nonzero overlaps result. These phonon-induced overlaps can be calculated by expanding the atomic $\langle 2p_\sigma | \varphi_{ns} \rangle$ overlaps and λ_σ in terms of nuclear displacements. Using the strain tensor components ϵ_{ij} and retaining only terms linear in ϵ_{ij}, we have

$$\langle \psi_u' | \varphi_{ns} \rangle \simeq -\frac{R}{\sqrt{3}} \left[\lambda_\sigma \frac{\partial S_{ns}}{\partial R} + S_{ns} \frac{\partial \lambda_\sigma}{\partial R} \right] (3\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})$$

$$\equiv a_{ns} (2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}),$$

$$\langle \psi_v' | \varphi_{ns} \rangle \simeq -R \left[\lambda_\sigma \frac{\partial S_{ns}}{\partial R} + S_{ns} \frac{\partial \lambda_\sigma}{\partial R} \right] (\epsilon_{xx} - \epsilon_{yy})$$

$$\equiv a_{ns} \sqrt{3} (\epsilon_{xx} - \epsilon_{yy}), \tag{2}$$

where R is the anion-cation distance, and $S_{ns} = \langle 2p_\sigma | \varphi_{ns} \rangle$. The overlap integrals with the occupied 1s, 2s, and 3s shells are accounted for by orthogonalizing the distorted orbitals ψ_u' and ψ_v' by the Schmidt process. The 4s function becomes admixed as a result of $2p_\sigma \to 4s$ transfer. Thus, the orthogonal antibonding orbitals perturbed by phonon excitation have the form

$$\psi_u'' = N(\Psi_u' - \sum_{n=1}^{3} \langle \psi_u' | \varphi_{ns} \rangle \varphi_{ns} + a_u \varphi_{4s});$$

$$\psi_v'' = N(\Psi_v' - \sum_{n=1}^{3} \langle \psi_v' | \varphi_{ns} \rangle \varphi_{ns} + a_v \varphi_{4s}), \tag{3}$$

where a_u, a_v are the 4s admixture coefficients, which are assumed to be the sum of two terms: the point-charge crystal-field admixture,[1] and a covalent transfer contribution. They have the same strain dependence as (2), so that we can define

$$a_u = -a_{4s} (2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy});$$

$$a_v = -a_{4s} \sqrt{3} (\epsilon_{xx} - \epsilon_{yy}). \tag{4}$$

Then the resulting phonon-induced hyperfine field is

$$H_{\mathrm{hf}} = (8\pi/3)\mu_{\mathrm{B}}[\langle\psi_u{}''|\delta(r)|\psi_u{}''\rangle + \langle\psi_v{}''|\delta(r)|\psi_v{}''\rangle]$$

$$\simeq \frac{8\pi}{3}\mu_{\mathrm{B}} \sum_{n=1}^{4} \sum_{n'=1}^{4} a_{ns}\cdot a_{n's}\langle\varphi_{ns}|\delta(r)|\varphi_{n's}\rangle 4(\epsilon_{xx}{}^2 + \epsilon_{yy}{}^2 + \epsilon_{zz}{}^2 - \epsilon_{xx}\epsilon_{yy} - \epsilon_{xx}\epsilon_{zz} - \epsilon_{yy}\epsilon_{zz}). \tag{5}$$

This field is parallel to the spin of the $3d^5$ ground state, and we obtain a net decrease of the total Mn^{2+} hyperfine field. By introducing the mean-square strains, $\langle\epsilon_{ij}{}^2\rangle$, we can express the temperature-dependent part of the hyperfine constant A as follows[1]:

$$A(T) = A(T=0)(1-CT^4)\int_0^{\theta/T} x^3 dx/(e^x - 1), \tag{6}$$

where θ is the averaged Debye temperature and

$$C = \frac{(8\pi/3)\mu_{\mathrm{B}}\sum_n \sum_{n'} a_{ns} a_{n's}\langle\varphi_{ns}|\delta(r)|\varphi_{n's}\rangle}{H_c} \times \frac{6\hbar}{5\rho\pi^2}\left(\frac{1}{v_t{}^5} + \frac{2}{3vl^5}\right)\left(\frac{k_{\mathrm{B}}}{\hbar}\right)^4, \tag{7}$$

where ρ is the mass density of the crystal, v_t and v_l are the transverse and longitudinal sound velocities, respectively, and H_c is the static hyperfine field coming from exchange polarization of the cores. We estimate the coupling parameters a_{ns} for Mn^{2+} in MgO as follows. Using Watson's Mn^{2+} free-ion wave functions for φ_{ns} and φ_u and O^{2-} wave functions[7] for $2p_\sigma$, we calculate the overlap integrals S_{ns} and $\langle 2p_\sigma|\varphi_u\rangle$ for various bond lengths. From these we deduce the values for $\partial S_{ns}/\partial R$ and $\partial\langle 2p_\sigma|\varphi_u\rangle/\partial R$ evaluated at the equilibrium anion-cation distance $R = 4.08$ a.u. In order to estimate $\partial\lambda_\sigma/\partial R$ we assume that λ_σ is proportional to $\langle 2p_\sigma|\varphi_u\rangle$. The proportionality constant can be deduced from the equilibrium value of λ_σ. A reliable experimental value of λ_σ is not available since the σ-ligand spin density contains an undetermined contribution from $2p_\sigma \to 4s$ transfer. The a priori calculations of Hubbard, Rimmer, and Hopgood[8] give $\lambda_\sigma = 0.28$ for $\mathrm{KMnF_3}$. The degree of covalency in oxides is expected to be stronger than in fluorides so that we estimate $\lambda_\sigma = 0.3$ for $\mathrm{Mn^{2+}}$:MgO. Since the $2p_\sigma \to 4s$ transfer matrix element cannot be reliably estimated we limit ourselves to calculating a_{4s} from the near-neighbor point-charge model. Using Rimmer's[9] wave function for $\mathrm{Mn}^+(4s)$ to evaluate $\varphi_{4s}(0)$ and inserting the values of ρ, v_t, and v_l appropriate to MgO crystal,[1] we find from Eq. (7) a strength constant $C = 1.24\times10^{-13}$ $(°\mathrm{K})^{-4}$ to be compared with $C_{\mathrm{exp}} = 2.58\times10^{-13}$ $(°\mathrm{K})^{-4}$ obtained by comparing Eq. (6) with the experimental values of Walsh, Jeener, and Bloembergen. If we neglect the covalency contributions of the $1s$, $2s$, and $3s$ shells, we obtain, for the near-neighbor point-charge $4s$ contribution, $C_{4s} = 0.38\times10^{-13}$ $(°\mathrm{K})^{-4}$ which is more than three times smaller than C estimated from Eq. (7). Therefore, a significant enhancement for the strength of the temperature dependence of A is obtained by taking into account the covalent admixture of inner shells. We can expect a further enhancement of a_{4s} caused by $2p_\sigma \to 4s$ transfer. Hence, a large part of the discrepancy between point-charge calculation and the experimental strength can be removed by the covalency effects.

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