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Theory of the transferred hyperfine interaction between well-separated atoms and the influence of soft-phonon modes

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We have calculated the transferred hyperfine interaction at the F^- ion in PbF_2 in which the distance between F^- and Pb^{2+} is 30% larger than the bond lengths in MnF_2. The contributions arising from the overlap of wave functions and the charge transfer and the charge redistribution effects have been calculated from first principles and the s, p_σ, and p_π spin densities have been found. The change in the transferred hyperfine coupling due to a soft-phonon mode which goes to zero at a temperature of $T_c = 50$ K has been calculated and verified experimentally.

I. INTRODUCTION

PbF_2 is a superionic lattice as the F^- sublattice has a lower melting point than that of the Pb^{2+} sublattice. The nuclear relaxation time of the ^{19}F nuclei in PbF_2 has been measured by Boyce *et al.*[1] and the electron paramagnetic resonance of the Mn^{2+} ion in this lattice by Evora and Jaccarino[2] and by Madrid *et al.*[3] The PbF_2 lattice is much larger in size than any other lattice in which the electron paramagnetic resonance of the Mn^{2+} ion has been studied so far. The Mn^{2+}-F^- distance in PbF_2 is 2.58 Å which is 28% larger than the 2.01 Å in LiF and 24% larger than the Mn^{2+}-F^- bond lengths of 2.10 and 2.13 Å in MnF_2 and 2.09 Å in $KMnF_3$. The ^{19}F transferred hyperfine coupling constants in PbF_2:Mn^{2+} are found[4] to be $A_s = 33.82$ MHz and $A_p = 7.82$ MHz. However, slightly different values, $A_s = 34$ MHz and $A_p = 6$ MHz, have been reported by Vernon *et al.*[5] Another characteristic of this lattice is that there is a soft-phonon mode, the frequency of which vanishes at a temperature of about 50 K so that the transferred hyperfine coupling shows a large reduction in its magnitude at this temperature with respect to its value at zero temperature. Since the electron frequency is larger than the hopping frequency $1/\tau_c$, of F^- diffusion, $\omega\tau_c \gg 1$, only the $M_s = -\frac{1}{2}$ to $+\frac{1}{2}$ transition of the Mn^{2+} ion is seen and the F^- sublattice melting is enhanced.

In our previous work, we have calculated[6-9] the transferred hyperfine interaction at the F^- site due to lattice vibrations in LiF:Mn^{2+}, KMgF:Mn^{2+}, MnF_2, and FeF_2 lattices. We have developed the complete theory for the transfer of an electron from an occupied orbital of an atom to an empty orbital of another atom. It was discovered that the transfer of an electron from one orbital to an empty orbital resulted in readjustment of charges leading to a contribution to the transferred hyperfine interaction. This calculation was reported[10-13] for three paramagnetic ions, V^{2+}, Cr^{3+}, and Cu^{2+} and their ion pairs with F^- as an intervening ion. The magnetic d electrons of the V^{2+} and Cr^{3+} ions transform like the T_{2g} irreducible representation of the octahedral group, representing π bonding with the F^- ion, whereas the magnetic electrons of Cu^{2+} transform like the E_g irreducible representation of the octahedral group and have σ bonds with the F^- ion. In β-KNO_3 the NO_3^- ions are rotating and vibrating so that there are liquidlike correlation times τ_c which create interesting hyperfine effects. The reduction in the hyperfine coupling of the Mn^{2+} ion due to such correlations has also been studied.[13]

In this paper, we present the theory of the transferred hyperfine interaction at the F^- ion due to both the σ-bonding and π-bonding electrons at the Mn^{2+} ion when the distance between the Mn^{2+} ion and the F^- ion is larger than in MnF_2 as appropriate to the Mn^{2+}-doped PbF_2 lattice. We also calculate for what may be the first time, the effect of a soft-phonon mode on the transferred hyperfine interaction for F^- near a Mn^{2+} ion in PbF_2. We find that our calculations are in accord with the experimental measurements[2-5] of magnetic resonance in Mn^{2+}:PbF_2.

II. STATIC THEORY

We first discuss the theory of the transferred hyperfine interaction[14] at the F^- ion site due to electrons at the Mn^{2+} ion with all the ions rigidly held in the lattice. We consider[15-17] the two-atom three-electron configuration a_1a_2-a_3 in which electrons 1 and 2 have their spins antiparallel and localized on one of the orbitals belonging to an F^- ion such as $2s$ or $2p$. The third electron belongs to an occupied orbital a_3 on a magnetic atom, Mn^{2+} in the present case which has a $3d^5$ configuration. The Hamiltonian of the system is given by

$$\mathscr{H} = \mathscr{H}_1 + \sum_{i,j} e^2/r_{ij} , \tag{1}$$

where e^2/r_{ij} is the repulsive Coulomb interaction between electrons and

$$\mathscr{H}_1 = -\frac{\hbar^2\nabla^2}{2m} - \sum_j Z_j e^2/r_{ij} \tag{2}$$

is the one-electron Hamiltonian containing the kinetic energy and the electron-nuclear attraction summed over all nuclei. We construct Slater-type wave functions for a system ψ_A which has $2p_\sigma$ orbitals doubly occupied with antiparallel spins and one occupied $d_{z^2\uparrow}$ orbital as

$$\psi_A = |p_{\sigma\uparrow} p'_{\sigma\downarrow} d_{z^2\uparrow}\rangle \ . \tag{3}$$

There are 3! such permutations because of spin permutations which are implied. We consider the transfer of an electron from the occupied $p'_{\sigma\downarrow}$ to the empty $d'_{z^2\downarrow}$ orbital which leaves behind an electron of up spin on the ligand atom. This *up* spin density is parallel to the d moment of the magnetic atom and hence may be termed the positive spin density at the ligand ion. The resulting configuration is given by

$$\psi_B = |p_{\sigma\uparrow} d_{z^2\uparrow} d'_{z^2\downarrow}\rangle \ . \tag{4}$$

As before, the spin permutations are implied. The perturbed ionic configuration is described by,

$$\psi'_A = \psi_A + \gamma\psi_B \ . \tag{5}$$

According to Serber's method,[18] the matrix elements between any two configurations such as ψ_{R_i} and ψ_{R_j} ($\psi_{R_i} = \psi_A$ or ψ_B) may be calculated from the expression

$$\mathscr{H}^{R_iR_j} = (2)^{(r_i - r_j)/2} \sum_P{}' \mathscr{H}^{R_iR_j} P^{R_iR_j} \ , \tag{6}$$

where $P^{R_iR_j}$ is the spin permutation operator. In our case

$$\gamma = \frac{\langle A\,|\mathscr{H}|\,B\rangle - \langle A\,|\,B\rangle\langle A\,|\mathscr{H}|\,A\rangle}{E_A - E_B} \ . \tag{7}$$

The matrix elements of any interaction, $\mathscr{H}$, between the configurations ψ_A and ψ_B each containing three electrons 1–3 are given by

$$\mathscr{H}^{AB} = -\mathscr{H}^{AB}_{13} \ . \tag{8}$$

In the notation,

$$\begin{aligned}
&\langle A\,|\mathscr{H}|\,A\rangle = \mathscr{H}^{AA}_I = E_A \ , \\
&\mathscr{H}^{BB}_I = E_B \ , \\
&\Delta_B = E_B - E_A \ , \\
&\langle A\,|\,B\rangle = S \ , \\
&\langle a_1a_2||a_3a_4\rangle = \left\langle a_1a_2 \left| \frac{e^2}{r_{ij}} \right| a_3a_4 \right\rangle \ ,
\end{aligned} \tag{9}$$

the transfer coefficient is given by

$$\begin{aligned}
\gamma = (&\langle a_1\,|\mathscr{H}_1|\,a_3\rangle - \langle a_1\,|\mathscr{H}_1|\,a_1\rangle S \\
&+ \langle a_3a_1||a_3a_3\rangle - \langle a_1a_3||a_1a_3\rangle S \\
&+ \langle a_1a_1||a_3a_1\rangle - \langle a_1a_1||a_1a_1\rangle S)\Delta_B^{-1} \ ,
\end{aligned} \tag{10}$$

where $\mathscr{H}_1$ is the single-electron Hamiltonian given by (2). We make linear combinations of d orbitals with $2s$ and $2p$ of the F^- ion as

$$\begin{aligned}
&\psi_e = N_e(d_\sigma - \lambda_s\chi_s - \lambda_\sigma\chi_\sigma) \ , \\
&\psi_t = N_t(d_\pi - \lambda_\pi\chi_\pi) \ ,
\end{aligned} \tag{11}$$

where ψ_e represents the d orbitals which transform like the E_{2g} irreducible representation of the octahedral group, χ_s are the linear combinations of the $2s(F^-)$ orbitals which transform like E_{2g}, and χ_p are those of the $2p$ orbitals which also transform like the E_{2g} irreducible representation. Similarly χ_π is the linear combination of $2p_x$ and $2p_y$ orbitals of the F^- ions which transform like the T_{2g} irreducible representation of the octahedral group. The three d_π orbitals also transform like the T_{2g} irreducible representation. The bonding orbitals which are orthogonal to (11) are given by

$$\begin{aligned}
&\chi'_s = \chi_s + \gamma_{s\sigma} d_\sigma \ , \\
&\chi'_\sigma = \chi_\sigma + \gamma_{p\sigma} d_\sigma \ , \\
&\chi'_\pi = \chi_\pi + \gamma_\pi d_\pi \ .
\end{aligned} \tag{12}$$

Up to the lowest order in γ the condition of orthogonality between (11) and (12) gives,

$$\begin{aligned}
&\lambda_s = \gamma_s + S_{\sigma s} \ , \\
&\lambda_\sigma = \gamma_\sigma + S_{p\sigma} \ , \\
&\lambda_\pi = \gamma_\pi + S_{p\pi} \ ,
\end{aligned} \tag{13}$$

where the overlap integrals are defined by

$$\begin{aligned}
&S_{\sigma s} = \langle d_\sigma\,|\,\chi_s\rangle \ , \\
&S_{p\sigma} = \langle d_\sigma\,|\,\chi_\sigma\rangle \ , \\
&S_{p\pi} = \langle d_\pi\,|\,\chi_\pi\rangle \ .
\end{aligned} \tag{14}$$

The transferred hyperfine interaction at the F^- site is described by the Hamiltonian $\mathscr{H} = \sum_i \mathbf{I}^i \cdot \mathbf{A} \cdot \mathbf{S}$, where I^i is the nuclear spin of the ith F^- ion and S is the electronic spin of the Mn^{2+} ion. The transferred hyperfine constant is determined from an isotropic component,

$$A_s = \frac{8\pi}{3} g\mu_B g_N \mu_N |\chi_s(0)|^2 f_s \tag{15}$$

and anisotropic components

$$\begin{aligned}
&A_\sigma = \frac{1}{S} g\mu_B g_N \mu_N \langle r^{-3}\rangle_\sigma f_\sigma \ , \\
&A_\pi = \frac{1}{S} g\mu_B g_N \mu_N \langle r^{-3}\rangle_\pi f_\pi \ ,
\end{aligned} \tag{16}$$

where the spin densities are given by

$$f_s = \lambda_s^2, \quad f_\sigma = \lambda_\sigma^2, \quad f_\pi = \lambda_\pi^2 \tag{17}$$

and g is the Landé splitting factor of the electron, $S = \frac{5}{2}$ for Mn^{2+}, g_N is the nuclear gyromagnetic ratio, μ_B is the Bohr magneton, and μ_N is the nuclear magneton. The average value of the radius vector of the $2p$ electrons of F^- occurs as $\langle r^{-3}\rangle$ which we calculate from the Hartree-Fock wave functions.

The dipole-dipole interaction between magnetic electrons and the nuclear spin of the ligand ions may be written as

$$\mathscr{H} = \sum_{i=1}^{5} g\mu_B g_N \mu_N \langle r_{ij}^{-3}\rangle [3(\hat{\mathbf{e}}_{ij} \cdot \mathbf{S}_i)(\hat{\mathbf{e}}_{ij} \cdot \mathbf{I}_j) - \mathbf{S}_i \cdot \mathbf{S}_j] \ , \tag{18}$$

where $\hat{\mathbf{e}}_{ij}$ is the unit vector in the direction from the jth nucleus F^- to the ith electron, $\mathbf{S}_i$ is the electron spin of Mn^{2+}, and $\mathbf{I}_j$ is the nuclear spin of F^-. In a cubic field two of the $3d^5$ electrons of Mn^{2+} transform as the E_{2g} irreducible representation while the remaining three electrons transform as the T_{2g} irreducible representation of the octahedral group so that the components of the transferred hyperfine interaction occur as given by (15) and (16). The effect of the electrons other than those included in the three-electron two-atom model (3) has been calculated in the point-charge model. A typical matrix element is calculated from the Hamiltonian

$$\mathscr{H}_1 = -\frac{\hbar^2}{2m}\nabla_1^2 + V_1(\mathrm{Mn}^{3+}) + V(\mathrm{F}^+) \, , \tag{19}$$

where V_1 (Mn^{3+}) and V (F^+) are effective one-electron Hartree potential energies. The valencies have been chosen such that the electron transfer already considered in (3) and (4) is not counted again. For example, the element $\langle a_1 | \mathscr{H}_1 | a_3 \rangle$ is calculated as

$$\begin{aligned}\langle a_1 | \mathscr{H}_1 | a_3 \rangle = \langle a_1 | & -\frac{\hbar^2\nabla^2}{2m} | a_3 \rangle \\ & + \langle a_1 | V_A(\mathrm{Mn}^{3+}) | a_3 \rangle \\ & + \langle a_1 | V(\mathrm{F}^+) | a_3 \rangle \, . \end{aligned} \tag{20}$$

The Hartree equation for the orbital a_1 is

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V(\mathrm{F}^+) + \left\langle a_2(r_2) \left| \frac{e^2}{r_{12}} \right| a_2(r_2) \right\rangle \right] | a_1(r_1) \rangle = E_H(\mathrm{F}^-) | a_1(r_1) \rangle \tag{21}$$

and for $| a_3 \rangle$ is

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V_1(\mathrm{Mn}^{3+}) \right] | a_3 \rangle = E_H(\mathrm{Mn}^{2+}) | a_3 \rangle \, . \tag{22}$$

Multiplying (21) by $\langle a_3 |$ and (22) by $\langle a_1 |$ and integrating we find

$$\begin{aligned}\langle a_3 | \mathscr{H}_1 | a_1 \rangle = E_H(\mathrm{F}^-)S - E_H(\mathrm{Mn}^{2+})S - \langle a_2 a_3 || a_2 a_1 \rangle \\ + \left\langle a_1 \left| \frac{\hbar^2\nabla^2}{2m} \right| a_3 \right\rangle \\ + \langle a_1 | V_1(\mathrm{Mn}^{3+}) | a_3 \rangle \, . \end{aligned} \tag{23}$$

The one-electron Hartree energies are given by Clementi[19] whereas the remaining integrals are calculated. It is found[20] that the effect of the exchange core polarization at the site of the F^- ion far separated from the Mn^{2+} ion is small.

III. COMPUTATIONAL RESULTS

The crystal structure of β-PbF_2 is described by Vernon *et al.*[5] Within a subunit cell Mn^{2+} is surrounded by eight F^- ions which are at the corners of a cube of side $a/2$ with $a = 5.96$ Å. The Mn^{2+}-F^- distance is $R = 2.58$ Å which is long compared with the Mn^{2+}-F^- distance in MnF_2. Therefore we take the distance R as a parameter as was done in previous cases.[10–12] We take the orbitals $a_1 = a_2 = 1s(F^-)$ and $a_3 = d_{z^2}(Mn^{2+})$ and compute all the integrals. The overlap integral $\langle 1s(F^-) | d_{z^2}(Mn^{2+}) \rangle$ along with some of the Coulomb integrals is plotted in Fig. 1, as a function of distance between Mn^{2+} and F^- ions. It is found that the Coulomb interaction plays a dominant role at large distances such as those found in PbF_2 as compared with MnF_2 where overlap dominates. The energies which are independent of the interatomic distance are $\langle 1s | \hbar^2\nabla^2/2m | 1s \rangle = -37.253$ a.u., $\langle d_{z^2} | \hbar^2\nabla^2/2m | d_{z^2} \rangle = 6.626$ a.u., and $\langle 1s\,1s || 1s\,1s \rangle = 5.357$ a.u. Next we take $a_1 = a_2 = 2s(F^-)$ and $a_3 = d_{z^2}(Mn^{2+})$. The computed values of the overlap integral $\langle 2s(F^-) | d_{z^2}(Mn^{2+}) \rangle$ and some of the Coulomb integrals are shown in Fig. 2 as a function of Mn^{2+}-F^- distance. The distance-independent values are $\langle 2s | \hbar^2\nabla^2/2m | 2s \rangle = -3.884$ a.u., $\langle 2s\,2s || 2s\,2s \rangle = 0.8834$ a.u. Again we see that Coulomb integrals dominate over the overlap effects. We construct the value of γ from (10) using $\Delta_B = -1.0$ a.u. and hence obtain the 2s spin density from (17) and (13). This value is plotted in Fig. 3 as a function of interatomic distance. For $4\pi | \varphi_{2s}(0) |^2 = 136.58$ a.u. the hyperfine constant of 2s

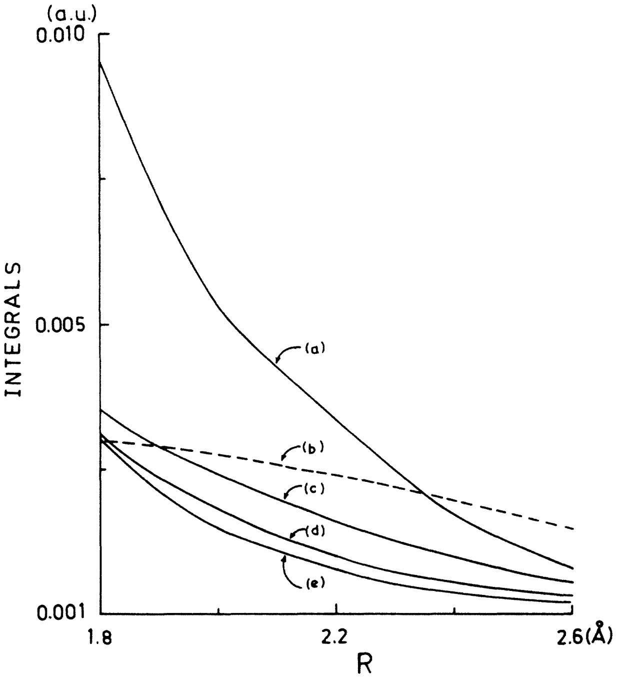

FIG. 1. Overlap integral between $1s(F^-)$ and $d_{z^2}(Mn^{2+})$ as a function of interatomic separation along with some of the Coulomb integrals as well as the split kinetic energy. (a) $\langle 1s | d_{z^2} \rangle$, (b) $\langle 1sd_{z^2} || 1sd_{z^2} \rangle \times 10^{-2}$, (c) $-\langle 1s | \hbar^2\nabla^2/2m | d_{z^2} \rangle$, (d) $\langle 1s\,1s || 1sd_{z^2} \rangle \times 10^{-1}$, and (e) $-\langle d_{z^2}1s || d_{z^2}d_{z^2} \rangle$. In the case of (b) and (d) the values have been divided by factors of 10^2 and 10 as indicated above to accommodate them on the same graph as the overlap, e.g., at $R = 1.8$ Å, $\langle 1sd_{z^2} || 1sd_{z^2} \rangle = 0.307$ a.u., etc. Note that (c) and (e) are negative.

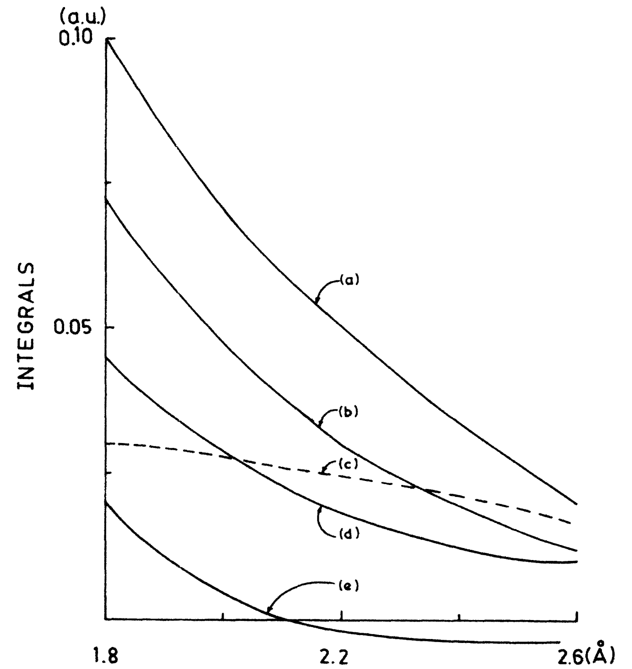

FIG. 2. Various integrals of $2s(\mathrm{F}^-)$ with those of $3d_z2(\mathrm{Mn}^{2+})$ in atomic units as a function of interatomic distance which is in Å. (a) $\langle 2s|d_{z^2}\rangle$, (b) $\langle 2s2s||2sd_{z^2}\rangle$, (c) $\langle 2sd_{z^2}||2sd_{z^2}\rangle\times 10^{-1}$, (d) $-\langle d_{z^2}2s||d_{z^2}d_{z^2}\rangle$, and (e) $-\langle 2s|\hbar^2\nabla^2/2m|d_{z^2}\rangle$. Note that split kinetic energy changes sign.

shell of F^- occupied by a single electron is given by $A_{2s}=(8\pi/3)[\,|\varphi_{2s}(0)|^2 g_N\mu_N/a_0^3]=16312$ G. Therefore the experimental value of 12 G corresponds to a spin density of 0.73×10^{-3}. This value is also shown in Fig. 3. The agreement between the calculated $2s$ spin density and the measured value[3] is quite reasonable as we have not included the $1s$ contribution. The amplitude of the $1s$ shell at the site of the F^- nucleus is $\varphi_{1s}(0)=14.58$ a.u. However, that of $2s$ is negative, $\varphi_{2s}(0)=-3.3$ a.u. Therefore,, it is important to consider the cross term between $1s$ and $2s$ spin densities. The isotropic spin density at the F^- is then defined by

$$f_s|\chi_s(0)|^2=f_{2s}|\varphi_{2s}(0)|^2+f_{1s}|\varphi_{1s}(0)|^2+2(f_{1s}f_{2s})^{1/2}\varphi_{1s}(0)\varphi_{2s}(0)\,. \qquad (24)$$

For an interatomic distance of 1.8 Å, the $1s$ atomic field is 1.8, the $2s$ field is 2.01, and the $1s,2s$ cross term is -1.9 a.u. Therefore, the effect of $1s$ shell is to reduce the $2s$ spin density by about 5%. Therefore, the theoretical value of the isotropic spin density is in reasonable agreement with the experimental value.

We now take $a_1=a_2=2p_\sigma(\mathrm{F}^-)$ and $a_3=d_{z^2}(\mathrm{Mn}^{2+})$ orbitals and calculate all the integrals, some of which are shown in Fig. 4. The calculated f_σ spin density is plotted in Fig. 5. The hyperfine constant of a $2p$ shell is given by $A_{2p}(0)=\frac{2}{5}g_N\mu_N\langle r^{-3}\rangle/a_0^3=458.98$ G, where we used $g_N=5.256$ for the nuclear gyromagnetic ratio of $^{19}\mathrm{F}$ and $\langle r^{-3}\rangle=6.405a_0^{-3}$ with the Bohr radius $a_0=0.529\times 10^{-8}$ cm and $\mu_N=5.0505\times 10^{-24}$ erg/G. The calculation is once again performed with $a_1=a_2=2p_\pi(\mathrm{F}^-)$ and $a_3=d_t(\mathrm{Mn}^{2+})$. Some of the integrals of which are shown in Fig. 6 and the resulting π spin density is given in Fig. 7. We find that the calculated values are in reasonable agreement with the experimental measurements.

The sign of the transferred hyperfine field at the F^- site calculated in the previous section is positive which means that the field at F^- is parallel to the $3d^5\uparrow\uparrow\uparrow\uparrow\uparrow$ mo-

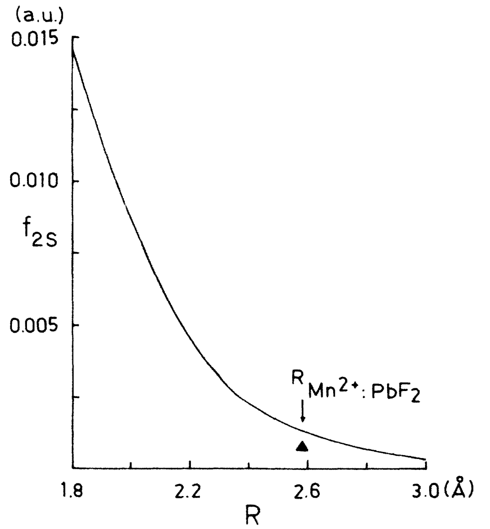

FIG. 3. f_{2s} spin density at the site of F^- ion as calculated as a function of interatomic distance. The Mn^{2+}-F^- separation as appropriate to PbF_2 is indicated by an arrow. The experimentally measured value (Ref. 3) is shown by a triangular point as discussed in the text.

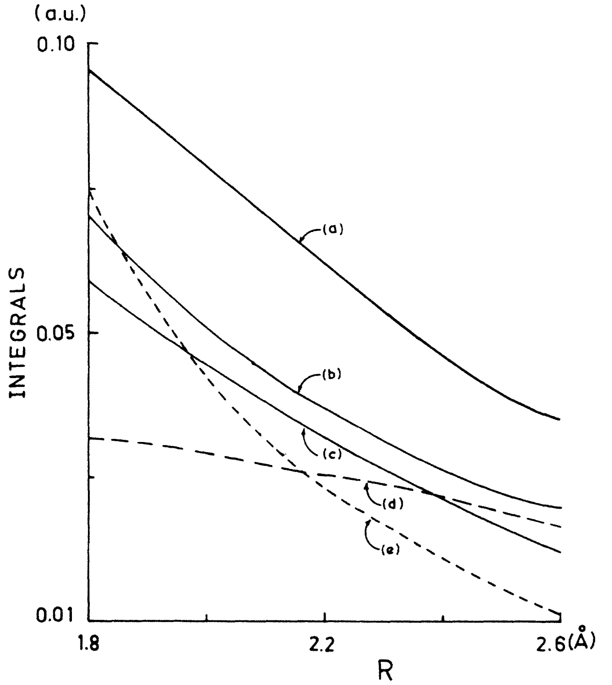

FIG. 4. Various integrals between $2p_\sigma(\mathrm{F}^-)$ and $d_{z^2}(\mathrm{Mn}^{2+})$. (a) $\langle 2p_\sigma|d_{z^2}\rangle$; (b) $\langle 2p_\sigma 2p_\sigma||2p_\sigma d_{z^2}\rangle$; (c) $-\langle d_{z^2}2p_\sigma||d_{z^2}d_{z^2}\rangle$; (d) $\langle 2p_\sigma d_{z^2}||2p_\sigma d_{z^2}\rangle\times 10^{-1}$; (e) $\langle 2p_\sigma|\hbar^2\nabla^2/2m|d_{z^2}\rangle$.

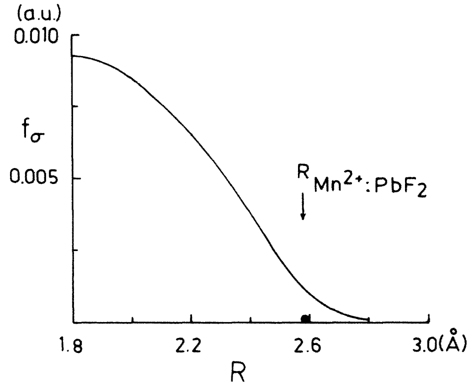

FIG. 5. Calculated p_σ spin density on the F^- ion as a function of interatomic distance. The distance as in PbF_2:Mn^{2+} is marked by an arrow. The point shows the experimental value.

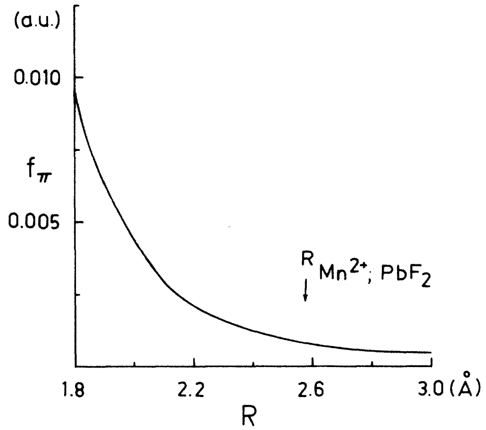

FIG. 7. π-electron spin density at the F^- site as a function of interatomic distance. The Mn^{2+}-F^- distance for PbF_2:Mn^{2+} is marked by an arrow.

ment. We visualize it as follows. First we consider $\uparrow\downarrow$-$\uparrow\uparrow\uparrow\uparrow\uparrow$ configuration in which the $2s(F^-)$ orbitals are doubly occupied with antiparallel spins and $3d^5$ electrons of the Mn^{2+} are spin up according to the Hund's ground state so that the total spin is $+\frac{5}{2}$. The $3d^5\downarrow\downarrow\downarrow\downarrow\downarrow$ orbitals are vacant so that when we consider the transfer of an electron from the $2s\downarrow(F^-)$ orbital to the empty $d\downarrow$ orbital of Mn^{2+}, there is a net up spin density at the F^- ion which is in the same direction as that of the occupied $3d^5\uparrow\uparrow\uparrow\uparrow\uparrow$ orbital. This is the positive transferred hyperfine interaction. There is an overlap between the $2s\uparrow(F^-)$ and $3d^5\uparrow$ orbitals so that because of the Pauli principle the $2s\uparrow(F^-)$ orbital is prevented from coming towards the $3d^5\uparrow$ orbitals so that the amplitude of the $2s\uparrow(F^-)$ orbital at the site of the F^- ion is increased relative to its value when the $3d^5\uparrow$ orbitals are not occupied. Therefore, there is a positive transferred hyperfine interaction due to the overlap effects. The overlap between the occupied $2s\uparrow(F^-)$ and occupied $3d^5\uparrow$ orbitals therefore leads to a positive transferred hyperfine interaction. The transfer of an electron from the occupied $2s\downarrow(F^-)$ to the empty $3d^5\downarrow$ orbitals also leads to positive transferred hyperfine interaction. However, a negative transferred hyperfine interaction may also arise so that the transferred hyperfine interaction arising from the transfer of $2s\downarrow(F^-)$ electrons to empty $3d\downarrow$ orbitals, discussed in the previous paragraph, may be reduced in magnitude. We imagine an arbitrarily small population on the otherwise empty $4s$ shell. The exchange interaction between the $4s\uparrow$ and $3d^5\uparrow$ orbitals is such that the $4s\uparrow$ orbital is energetically favored over the $4s\downarrow$ orbital. Therefore the $2s\uparrow(F^-)$ to $4s\uparrow$ transfer is favored rather than the $2s\downarrow(F^-)$ to $3d\downarrow$. This leads to a net downward negative spin at the $2s(F^-)$ site. Therefore an excitation of the $2s\uparrow(F^-)$ electron to the empty $4s\uparrow$ orbital leads to a reduction of the transferred hyperfine interaction.

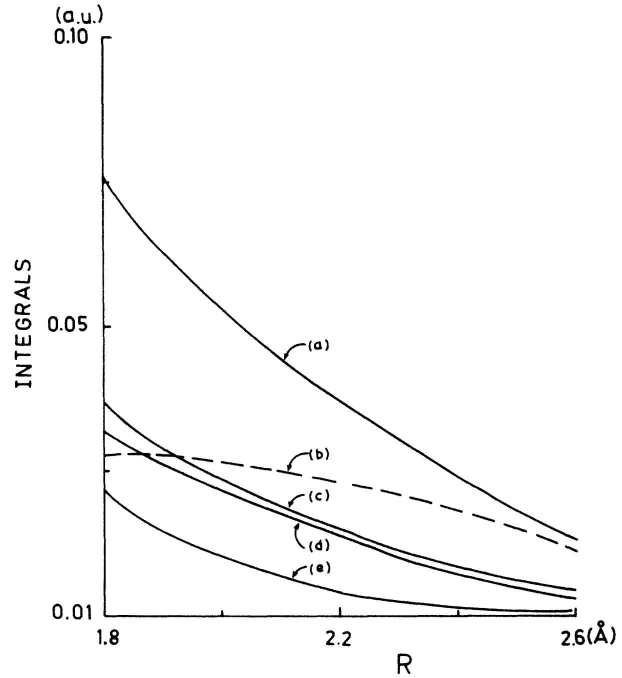

FIG. 6. π-electron integrals including the overlap, the split kinetic energy and some of the charge redistribution integrals in atomic units. (a) $\langle 2p_\pi | d_t \rangle$, (b) $\langle 2p_\pi d_t || 2p_\pi d_t \rangle \times 10^{-1}$, (c) $\langle 2p_\pi 2p_\pi || 2p_\pi d_t \rangle$, (d) $\langle d_t 2p_\pi || d_t d_t \rangle$, and (e) $-\langle 2p_\pi | \hbar^2 \nabla^2 / 2m | d_t \rangle$. Note the scale multiplication, e.g., at $R = 1.8$ Å, $\langle 2p_\pi d_t || 2p_\pi d_t \rangle = 0.286$ a.u.

IV. SOFT-PHONON MODE IN TRANSFERRED HYPERFINE COUPLING

We consider a small distortion or contraction of the F^- ions which surround the Mn^{2+} ion. When this contraction goes to zero, the lattice expands and we expect the transferred hyperfine interaction to decrease in magnitude. The frequency of a phonon then goes to zero at a temperature of about $T_c = 50$ K. A soft-phonon mode in PbF_2 has indeed been reported.[21] We calculate the positive transferred hyperfine interaction due to the transfer of an electron from the occupied $2s\downarrow(F^-)$ to the empty $3d\downarrow$ orbital. The potential energy from the modulation of the electron-nuclear attraction may be written as

$$\mathscr{H}'=\sum_i \delta R_i \frac{\partial}{\partial R_i} Z_i e^2/r_{ij}=\sum_n V_n Q_n \ , \tag{25}$$

where V_n is the derivative of the potential with respect to the radius vector of the ith atom and Q_n is the nth normal coordinate. The interaction (25) was first written by van Vleck[22] in connection with their studies of the spin-lattice relaxation times of paramagnetic atoms in insulating materials. The transfer coefficient (10) now has an additional term of the form,

$$\gamma_{\mathrm{soft}}=\Delta_B^{-1}\left[\left\langle a_1 \left| \sum_n V_n \right| a_3\right\rangle-\left\langle a_1 \left|\sum_n V_n \right| a_1\right\rangle S\right] Q_n \ , \tag{26}$$

where the displacement operator is given by

$$Q_n=|\hat{n}| \left[\frac{\hbar}{2M\omega_{\mathbf{k}}}\right]^{1/2} |\mathbf{k}| (a_{\mathbf{k}}+a^{\dagger}_{-\mathbf{k}}) \ . \tag{27}$$

Here $|\hat{n}|$ selects a particular normal mode of the lattice[22,23] at which the symmetry breaks, M is the mass of the crystal, $\omega_{\mathbf{k}}$ the phonon frequency with $|\mathbf{k}|$ as the wave vector, and $a^{\dagger}_{\mathbf{k}}$ and $a_{\mathbf{k}}$ are the creation and annihilation operators for the phonons. We introduce[24] an order parameter Δ which vanishes when the distortion is released[25] at a particular temperature T_c analogous to the Peierls temperature such that

$$\langle a_{\mathbf{k}}+a^{\dagger}_{-\mathbf{k}}\rangle=\frac{\Delta}{V_n}\delta_{k,Q} \ , \tag{28}$$

where $Q=\pi/a$ is at the zone. The transferred hyperfine interaction is then found to be,

$$A_{2s}=\frac{8\pi}{3} g\mu_B g_N \mu_N |\chi_s(0)|^2 (S+\gamma+\gamma_{\mathrm{soft}})^2 \tag{29}$$

when γ_{soft} goes to zero, the transferred hyperfine coupling changes by

$$\delta A_s=\frac{8\pi}{3} g\mu_B g_N \mu_N |\chi_s(0)|^2 [\gamma_{\mathrm{soft}}^2-2(S+\gamma)\gamma_{\mathrm{soft}}] \ , \tag{30}$$

where

$$\gamma_{\mathrm{soft}}=\Delta_B^{-1}(\langle 2s\downarrow | V_n | d\downarrow\rangle - \langle 2s\downarrow | V_n | 2s\downarrow\rangle S) \left[\frac{\hbar}{2M\omega}\right]^{1/2} \frac{\pi\Delta}{aV_n} \ . \tag{31}$$

Since the matrix elements of the derivatives of the crystal potential are difficult to estimate theoretically we give the value as deduced from the experimental measurements which is $\delta A_s=3.54$ G. As the distortion is relaxed at $T_c=50$ K, the δA_s approaches zero as shown in Fig. 8. At zero temperature there is a finite charge-density surplus at $3d^6$ configuration with a deficiency at F^- which is released at T_c where the charge is closer to that of $3d^5$. Thus there is a local charge adjustment associated with a soft-phonon mode. The value of 50 K is in the range usually expected for a Peierls distortion. At present the measurements[3] of A_s for PbF_2:Mn^{2+} are available which we have used in Fig. 8. However, good measurements of the temperature dependence of A_σ and A_π have yet to be carried out.

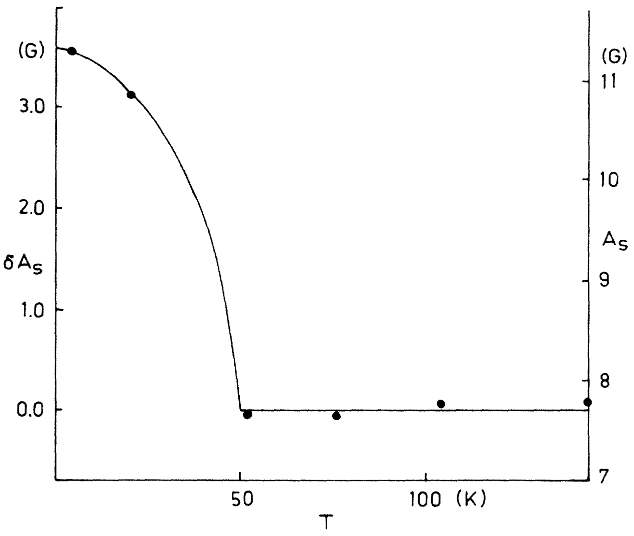

FIG. 8. Soft-phonon contribution to the isotropic component of the transferred hyperfine coupling δA_s which goes to zero at $T_c=50$ K. The full value of A_s is also shown on the right-hand side in gauss as a function of temperature. The dots are the experimental points taken from the work of Madrid *et al.* (Ref. 3). The theoretical value is ours as discussed in the text.

V. CONCLUSIONS

We have calculated the static transferred hyperfine coupling at the $^{19}F^-$ ion site in the neighborhood of Mn^{2+} ion from the first principles. The isotropic component of the transferred hyperfine interaction is in reasonable agreement with the experiments. We have also predicted the change in the transferred hyperfine constant which occurs at the F^- ion site as a result of charge transfer from the $2s(F^-)$ to the empty $3d^6$ orbital resulting in a charge accumulation at the Mn^{2+} site and hence a lattice distortion. When the temperature is varied at a particular temperature, $T_c=50$ K, the charge accumulation is relaxed. The predictions of our theory are in complete accord with the experiments.

Although the theory of the static transferred hyperfine interaction was described by Watson and Freeman[14] and Simanek and Sroubek,[26] it had been improved by Hubbard *et al.*[27] by considering the configurational interaction rather than one-atom orbitals for the calculation of charge transfer. In the two-center three-orbital model, the advantage is that the molecular-orbital charge transfer can be written in terms of two-center integrals for computational convenience. It is completely equivalent to the Hubbard[27] scheme except that now all possible combinations of the wave functions can be made for determining the charge transfer. Thus the theory of 1960s is now considerably improved.[10–12] The PbF_2 lattice has a much larger lattice constant than MnF_2. We have calculated all the integrals using Hartree-Fock wave functions as a function of interatomic distance which suggests that the transferred hyperfine constant varies approximately as R^6. Thus the importance of the distance dependence of the transferred hyperfine coupling is quite clear as we can then follow the changes in going from one lattice to another. Mishra *et al.*[28] have considered the effect of changing ligands, such as Cl^- in place of Br^-, on the hyperfine fields using unrestricted Hartree-Fock wave functions in which the basis functions are expressed as linear combination of primitive Gaussian functions. As the size of the lattice itself changes in going from the chloride to the bromide lattice, there is considerable change in the hyperfine field owing to distances themselves as found by us.[29] Thus the two effects, namely, that of the chemical change of the ligand ions and that of distances have to be distinguished. Ours may be the first calculation of the changes as a function of distance.

It is of interest to point out the spin dependence of the problem. The occupied $3d^5$ orbitals are of ↑ spin and the energetically favorable empty $4s$ orbitals are also ↑ spin. A transfer of an electron from the $2s\uparrow(F^-)$ to $4s\uparrow$ orbital gives rise to a reduction of ↑ spin density at F^- ion. This effect has been estimated to be about six percent of the experimental value of the transferred hyperfine interaction but plays an important role[9] when $2s\uparrow(F^-)$-to-$4s\uparrow$ transfer is induced by phonons in the form of a temperature-dependent reduction.

In conclusion, we have developed the static theory of the transferred hyperfine interaction with all the possible diagrams taken into account. We have calculated the interatomic distance dependence of the charge transfer integrals for the first time. We have also studied the effect of the soft phonon on the transferred hyperfine interaction for the first time.

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