Theory of transferred hyperfine interaction in σ-bonding systems: Cu^{2+} ion and $Cu^{2+}F^-Cu^{2+}$ pair

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The theory of transferred hyperfine interaction at the F^- site in the σ-electron systems $Cu^{2+}F^-$ and $Cu^{2+}F^-Cu^{2+}$ in cubic crystals is developed from the first principles. The transfer of the σ electron from the occupied p and s orbits of F^- to the empty d_{z^2} orbit on the Cu^{2+} ion is considered and all the integrals of the kinetic energy and Coulomb terms are evaluated using Hartree-Fock wave functions. The spin density in the case of one Cu^{2+} ion is found to be different from that in the Cu^{2+} ion-pair case. The s-spin density is found to vary with the interactomic distance as $R^{-5.63}$ in the pair case. The variation of the p_σ spin density with interatomic separation is rather involved. As the $Cu^{2+}F^-$ distance is increased from 1.8 Å, the p_σ spin density first decreases going through a minimum at about $R = 2.0$ Å and is almost independent of distance from $R = 2$ Å to $R = 2.1$ Å. For R larger than about 2.2 Å this spin density decreases monotonically with increasing distance. The isotropic as well as the anisotropic transferred hyperfine coupling are calculated.

I. INTRODUCTION

In transferred-hyperfine-interaction theories several effects have been discussed, the easiest of these being the overlap contribution between the orbits of the ligand ion and those of the magnetic ion. In the calculations which have been performed, this overlap effect accounts only for a small fraction of the experimentally observed spin density. Besides, the calculations have been done only for the Mn^{2+} ion which has both T_{2g}- and E_g-type orbitals. It has been suggested that the exchange interaction of the spin-up and -down electrons of the ligand ion with the unpaired electrons of the magnetic ion gives rise to the unpaired spin density at the site of the ligand ion. However, the only calculation[1] of this kind of transferred hyperfine interaction gave a zero result because of both positive and negative contributions. The transfer of electrons from the occupied orbits on the ligand to the empty orbits of the magnetic ion is believed to give an important contribution to the transferred hyperfine interaction. Since this effect is very difficult to calculate, some authors[2] have proposed to estimate this contribution by scaling the overlap contribution. The role of spin polarization[3] and consideration of empty orbits has now been well recognized in connection with this problem.

The mechanisms of exchange and superexchange have been studied[4] but the importance of these calculations to the problem of transferred hyperfine interaction has not been appreciated, though it is known[5] that this type of mechanisms does change the hyperfine coupling of the magnetic ion by a small amount.

In order to keep the problem sufficiently under control, we considered it important to first discuss a system with E_g ground state. The electronic configuration of Cu^{2+} is $3d^9$. In a cubic crystal the only hole in the $3d$ orbit is of E_g type. This ion also forms interesting[6] fluorides such as K_2CuF_4 which has the ions Cu^{2+}-F^--Cu^{2+} arranged in a straight line. Accordingly, we present the first theory of transferred hyperfine interaction in the E_g ground state. Proper consideration of the Cu^{2+}-F^--Cu^{2+} pair leads to a new charge-rearrangement contribution to the transferred hyperfine coupling at the F^- ion site. We consider the transfer of electrons from the occupied orbitals of the F^- to the empty hole on the Cu^{2+} ion and give a complete calculation of all the integrals involved as a function of internuclear distance. In this calculation it is found that whereas the s spin density at the F^- site monotonically decreases with increasing distance, the p spin density shows a rather interesting behavior. First it decreases with increasing distance going through a shallow minimum at a $Cu^{2+}F^-$ separation of about 2 Å, remaining almost flat from $R = 2.0$ to about 2.1 Å. For $R > 2.1$ Å, this p spin density decreases again with increasing separation. The flat region in the case of the single-Cu^{2+} ion is a bit larger than in the case of the pair. The minimum may be indicative of $Cu^{2+}F^-$ molecule formation, since it is at this distance that the charge-rearrangement contribution changes sign. In the flat region, the charge does not have to be significantly perturbed to rearrange the atoms. In K_2CuF_4 there are[6] two types of $Cu^{2+}F^-$ bonds, one $Cu^{2+}F^-$ separation is 1.95 Å and the other 2.08 Å. These values are within the range expected from our first-principles theory. As far as we know,

this is the first time that such a behavior is found in spin-density calculations. This is also the first time that a calculation has given some idea of the equilibrium distance between two atoms in a solid.

II. THEORY

The electronic configuration of Cu^{2+} is $3d^9$. In a cubic crystal field the ground state transforms as the E_g representation of the octahedral group. In order to study the $Cu^{2+}F^-Cu^{2+}$ linear pair, we consider the four-orbital models, e.g., $d_{z^2}(4)$-$p_\sigma(1)p_\sigma(2)$-$d_{z^2}(3)$.

Since the calculation of one follows from the other, we consider the configuration a_4-a_1a_2-a_3. For this purpose, a_1 and a_2 represent p_σ electron orbitals of the F^- ion and can be replaced by b_1 and b_2 representing the s function of the F^- ion, a_3 and a_4 represent the d_{z^2} orbitals on the Cu^{2+} ion at the right and left, respectively. The ionic configuration and the configuration with transfer of an electron from any of the two p_σ or s orbitals to the atom on the left or on the right are considered the same way as in the case of T_{2g} state[7] using the Serber method.[8,9] In the case of the a_4-a_1a_2-a_3 system of orbitals, the pair charge-transfer coefficient is found to be

$$\gamma_2 = [\ \langle a_1|H_1|a_3\rangle - \langle a_1|H_1|a_1\rangle S + \langle a_3a_1||a_3a_3\rangle + \langle a_1a_4||a_3a_4\rangle + \langle a_1a_1||a_1a_3\rangle$$
$$- \langle a_1a_1||a_1a_1\rangle S - (\langle a_1a_4||a_1a_4\rangle + \langle a_1a_3||a_1a_3\rangle + \langle a_3a_4||a_3a_4\rangle)S]\Delta_B^{-1}\ ,$$

where we have used the notation of Ref. 7. If we work for F^--Cu^{2+} represented by a_1a_2-a_3 orbitals we obtain

$$\gamma_1 = (\langle a_1|H_1|a_3\rangle - \langle a_1|H_1|a_1\rangle S + \langle a_3a_1||a_3a_3\rangle$$
$$- \langle a_1a_3||a_1a_3\rangle S + \langle a_1a_1||a_3a_1\rangle - \langle a_1a_1||a_1a_1\rangle S)\Delta_B^{-1}\ ,$$

for the electron transfer from F^- to Cu^{2+} corresponding to FCu^+. For convenience of computation we define

$$\gamma_1 = \gamma_{11} + \gamma_{12}, \quad \gamma_{11} = (\langle a_1|H_1|a_3\rangle - \langle a_1|H_1|a_1\rangle S)\Delta_B^{-1}\ ,$$

$$\gamma_{12} = (\langle a_1a_3||a_3a_3\rangle + \langle a_1a_3||a_1a_3\rangle S + \langle a_1a_1||a_3a_1\rangle - \langle a_1a_1||a_1a_1\rangle S)\Delta_b^{-1}\ .$$

Comparing the pair γ_2 together with the one $-$ Cu^{2+}-ion γ_1, we see that in the pair case the electron transferred from F^- to one Cu^{2+} returns to another Cu^{2+} because of Coulomb interaction and there is a charge redistribution induced by the transfer. We separate this contribution,

$$\gamma_c = (\ \langle a_1a_4||a_3a_4\rangle + \langle a_1a_4||a_1a_4\rangle S)\Delta_B^{-1}\ ,$$

$$\gamma_2 = \gamma_1 + \gamma_c\ .$$

We use the Hartree-Fock wave functions of Cu^{2+} and F^- as given by Clementi and Roetti.[10] Tables I and II give the estimates of the overlap and charge-transfer

parameters.[11] We use atomic units except when mentioned otherwise. The coefficient γ_1 refers to one Cu^{2+} ion and one F^- ion and γ_2 refers to the pair of Cu^{2+} ions with F^- in between. The spin densities are defined as

$$f_1^s = (S_s + \gamma_1^s)^2\ , \quad f_1^\sigma = (S_\sigma + \gamma_1^\sigma)^2\ ,$$

$$f_2^s = (S_s + \gamma_2^s)^2\ , \quad f_2^\sigma = (S_\sigma + \gamma_2^\sigma)^2\ ,$$

with the subscripts and superscripts s and σ depending on which orbital of the F^- ion one uses. Only $2s$ and $2p$ functions of the F^- are used. The $1s$ functions are neglected since their contribution is small.

TABLE I. Transfer coefficients and overlap for $F^-(s)$ for one Cu^{2+} and for the linear pair as a function of $Cu^{2+}F^-$ separation (atomic units).

R	3.4015	3.590	3.779	3.968	4.157	4.346
γ_{12}^s	0.024306	0.021276	0.018373	0.015704	0.013281	0.011145
γ_{11}^s	-0.00460	-0.00165	-0.00017	-0.00127	-0.00185	-0.00209
γ_1^s	0.019706	0.019626	0.018203	0.014434	0.011433	0.009055
S	0.066407	0.054714	0.044796	0.036535	0.029647	0.023959
γ_c^s	-0.001472	-0.001628	-0.002521	-0.003394	-0.004265	-0.005002
γ_2^s	0.018233	0.017998	0.015682	0.011040	0.007168	0.004054

TABLE II. Transfer coefficients and overlap for $F^-(2p)$ for one Cu^{2+} ion and the Cu^{2+} pair as a function of interatomic distance (atomic units).

R	3.401	3.590	3.779	3.968	4.157	4.346
γ_{12}^σ	0.031454	0.029706	0.024527	0.025682	0.023529	0.021353
γ_{11}^σ	−0.0247	−0.0180	−0.0131	−0.0093	−0.0065	−0.0045
γ_1^σ	0.006754	0.011706	0.011457	0.016342	0.017029	0.016853
S_σ	0.07232	0.06432	0.05078	0.04982	0.04350	0.037845
γ_c^σ	0.007792	0.003556	−0.000016	−0.003466	−0.006175	−0.008249
γ_2^σ	0.014546	0.015262	0.011441	0.012876	0.010854	0.008603

The one-electron Hartree energies and pertinent data are taken from Ref. 10 and the effect of ions other than those considered is calculated within the point-charge model.[9] The denominator is estimated to be $\Delta_B = -1.0$ a.u. The approximation scheme and the computer programs used are the same as in Refs. 4, 7, and 9. The calculation is performed as a function of $Cu^{2+}F^-$ separation. In the case of the $2s$ spin density it is found that the variation is of the order of $R^{-5.45}$ in the single-ion case compared with $R^{-5.63}$ in the pair case. For an octahedral cluster the values of f_1^s should be multiplied by a factor of 6. Thus for $R = 3.779$, $a_0 = 2$ Å, we obtain $f_1^s \simeq 2.4\%$. In the case of a paramagnetic pair $f_2^s \simeq 0.7\%$, it is double this value for a ferromagnetic pair, and zero for anti-ferromagnetic coupling. The dependence of the p spin density on the internuclear distance is much more complicated than for s character. Accordingly, this behavior is shown in Fig. 1 for both the single-Cu^{2+}-ion case f_1^σ and for the pair f_2^σ. It is found that there is a shallow minimum at about $R = 2$ Å, there is a flat region from $R = 2$ Å to $R = 2.2$ Å in

the single-Cu^{2+}-ion case and from 2 to 2.1 Å in the pair case. This is perhaps associated with molecule formation since this range is found in naturally occurring fluorides of the Cu^{2+} ion. The step character of the σ spin density in this region also shows that the atoms can be moved around 0.1 Å with arbitrary small energies without distributing the charge configuration seriously. It may be that it is because of this character that the displacive Jahn-Teller effect is commonly found in Cu^{2+} compounds. Apart from the Hartree-Fock wave functions and simple consideration of charge and spin, nothing else has been included in our theory. Thus it appears that we have given an interesting theory of the spin density at the F^- ion in σ bonding systems. The minimum is a consequence of cancellations and sign reversals that occur in our theory.

The transferred hyperfine interaction, $\mathcal{H} = IAS$, with S the atomic spin at the Cu^{2+} ion and I the nuclear spin of the $^{19}F^-$ ion, can be written as an isotropic contribution and an anistropic contribution which are related to the spin density as

$$A_s = A(0)f_s ,$$

$$A_\sigma = A_\sigma(0)f_\sigma ,$$

where

$$A_s(0) = \tfrac{1}{3}(8\pi)g\mu_B g_N \mu_N |\psi_s(0)|^2 ,$$

$$A_\sigma = g\mu_B g_N \mu_N \langle r^{-3} \rangle .$$

Thus the calculation of f_s and f_σ implies the calculation of transferred hyperfine interaction. In the case of the F^- ion

$$|\psi_{2s}(0)|^2 = 10.73a_0^{-3}, \quad \langle r^{-3} \rangle = 6.405a_0^{-3} ,$$

$g_N = 5.256$, for Cu^{2+}, $g \simeq 2$, and the remaining constants are

$$a_0 = 0.529\,177 \times 10^{-8}\ \text{cm},$$

$$\mu_B = 9.2732 \times 10^{-21}\ \text{erg}\ G^{-1} ,$$
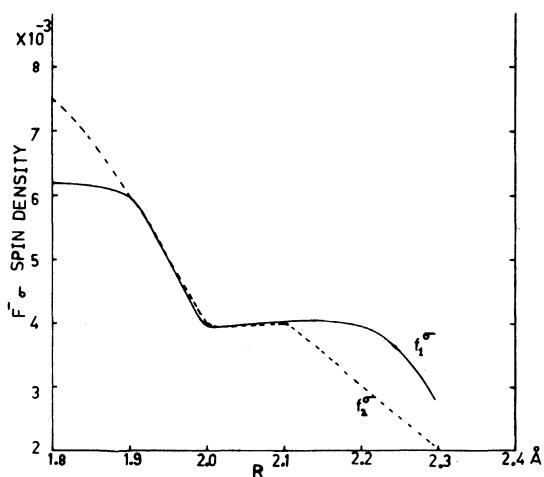
$$\mu_N = 5.0505 \times 10^{-24}\ \text{erg}\ G^{-1} ,$$

FIG. 1. Variation of spin density f_1^σ for one Cu^{2+} ion and f_2^σ for the pair as a function of $Cu^{2+}F^-$ separation.

so that

$$A_s(0) = 1400.292 \times 10^{-4} \text{ cm}^{-1},$$

and

$$A_\sigma(0) = 1070.59 \times 10^{-4} \text{ cm}^{-1}.$$

For $f_1^s = 2.4\%$, after dividing the result by hc to have the desirable units we find $A_s \simeq 33.6 \times 10^{-4}$ cm^{-1}, and for $f^\sigma = 2.34\%$ for an octahedral system at $R = 3.78$ a_0, we predict $A_\sigma = 25.05 \times 10^{-4}$ cm^{-1}. Thus we obtain the transferred hyperfine interaction from first principles.

A word of caution may be added about the uncertainty in the value of $-\Delta$. The value of 1 a.u. has been obtained by considering the "unoccupied" energy of the Cu^{2+} ion, the ionization energy of the F^- ion, the increase in the Madelung energy together with the electron-hole interaction energy subsequent to charge transfer, as suggested by Hubbard et al.,[12] and the static electronic polarization energy reduced by a factor of 3 to take into account the reduction due to many-body interactions.[9] The difficulty in estimating this charge-transfer energy has also been discussed in the calculation of the exchange interaction[13] where it has rather serious consequences on the cancellations. In our problem Δ occurs only in the denominators so that the values of γ can be easily deduced for any other choice of the value of Δ. In many-body theories the Coulomb interactions are screened by strong correlations. In the free-electron gas the correlations are about as strong as the Hartree-Fock energy so that the reduction factor is about 2. In the solid the correlations are stronger than in the gas depending upon the electron density

so that our reduction factor of 3 may be a reasonable approximation.[9] This difficulty in estimating the charge-transfer energy has been experienced in all previous calculations and it has been a custom to rely only on the overlap integral ignoring the transfer completely. In fact in connection with the calculations of the transferred hyperfine interaction ours are amongst the fewest efforts to calculate γ and we think the estimates are reasonably correct.

III. CONCLUSIONS

We have calculated the transferred hyperfine interaction in $Cu^{2+}F^-$ and $Cu^{2+}F^-Cu^{2+}$ from Hartree-Fock wave functions. We find that in going from one Cu^{2+} ion to the Cu^{2+}-ion pair the spin density is altered because of charge redistribution. We have calculated the spin density as a function of internuclear distance and find that the s spin density goes approximately as $R^{-5.5}$. On the other hand the σ spin density shows a shallow minimum at about the $Cu^{2+}F^-$ separation of 2 Å. Near this separation the atoms can be displaced by small energies without altering the charge distribution significantly. Thus Cu^{2+} systems could be sensitive to small perturbation arising from any source. It is perhaps for this reason that the displacive Jahn-Teller effect is a common finding in Cu^{2+} salts. In K_2CuF_4 there are two types of $Cu^{2+}F^-$ bonds, one of the length 1.95 Å and the other of 2.08 Å. This is just the region where we predict displacement of atoms without significantly altering the charge distribution. It may thus be of interest to look for soft phonon modes[14] in Cu^{2+} salts through Raman scattering of light.

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