

Theory of the Nuclear Magnetic Resonance Shift in Paramagnetic Crystals*

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A theoretical study is made of the shift of the F^{19} nuclear resonance in paramagnetic and antiferromagnetic MnF_2 which has been observed by Shulman and Jaccarino. The problem is reduced to that of a single $Mn-F$ pair. A net hyperfine interaction is shown to arise from overlap effects in the ground-state ionic configuration $(3d)^5(2s)^2(2p)^6$ and from overlap and transfer effects to the configurations $(3d)^6(2s)(2p)^6$ and $(3d)^6(2s)^2(2p)^5$. These three configurations are equivalent to a single configuration involving bonding-type molecular orbitals. The results are in reasonable agreement with the experiment, the theoretical isotropic shift being slightly too small and the theoretical anisotropic shift (small nondipolar part) being slightly too large. A re-appraisal is made of Tinkham's data on paramagnetic resonance of Mn^{++} impurities in ZnF_2 , which Bleaney has shown to be closely related to the Shulman-Jaccarino data. It is found that there is no need to include, as did Tinkham, a large fraction of fluorine $3s$ and $3p$ functions into the bond.

I. INTRODUCTION

SHULMAN and Jaccarino¹ (SJ) have recently succeeded in measuring the nuclear F^{19} resonance in the paramagnetic state of a single crystal of MnF_2 , and they find that the resonance frequency is shifted from the free-ion F^- value by a surprisingly large internal field. In this paper we examine various possible causes of the SJ resonance shift.

The experimental results of SJ can be summarized as follows: In the paramagnetic state of MnF_2 , in an applied field H_0 parallel to the c axis, or $[001]$ direction, the nuclear F^{19} resonance can be fitted by the relation

$$\omega = \gamma_N(H_0 + \Delta H), \quad (1)$$

with ΔH , as a function of temperature, directly proportional to the paramagnetic susceptibility χ . When H_0 is rotated in the (001) plane, the average resonance frequency is the same as with H_0 along c , and there is in addition a small anisotropic term.

Part of the effective field entering into ΔH is of course the dipolar field (including demagnetizing effects) coming from the paramagnetic Mn^{++} ions. This has been calculated by Smilowitz,² and the results are quoted in Appendix A of SJ.

The observed value of ΔH is found to be linear in H_0 , as required for dipolar fields in a paramagnet. The dipolar fields account for nearly all of the anisotropic term but are an order of magnitude too small to explain the large average shift. After subtracting the calculated dipolar field from the measured average ΔH , SJ are left with

$$(\Delta H/H_0) = 0.0735 \pm 0.0003, \quad (2)$$

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¹ R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1957).

² B. Smilowitz (private communication).

at 77°K. It is this large nondipolar average shift, and also the small remainder of the anisotropic shift, which we propose to explain.

We shall show that the overwhelming contribution comes from a net hyperfine interaction accompanying overlap effects between F^- and Mn^{++} ions in the ground-state nearly-ionic configuration of the crystal. Very briefly, the mechanism is as follows: Consider an Mn^{++} ion with magnetic moment up. The $3d$ electrons will automatically be orthogonal to the down neighbor fluorine electrons (that is, electrons with magnetic moments down), but not to the up fluorine electrons. As a consequence the up electrons, in the crystal, will no longer exactly pair off with the down electrons—that is, their crystalline orbitals will differ. This results in a net internal magnetic field at the F^{19} nucleus. We shall speak of an “effective fraction” f of an unpaired fluorine electron as being responsible for this field. The field will fluctuate at a rate corresponding to the Mn^{++} spin-relaxation frequency, which is very rapid compared to the nuclear resonance frequency. The nucleus will therefore see an average field which will be proportional to the excess of Mn moments in the direction of H_0 , or directly proportional to χ .

As has been discussed by SJ, we may picture this effect in terms of antibonding molecular orbitals. But we may also take the atomic-orbital point of view and think of overlap effects in the ground $Mn^{++}F^-$ state and transfer effects to the excited Mn^+F state. In Sec. VI it is shown that these two points of view, molecular orbitals and atomic orbitals, lead to the same theoretical predictions.

Bleaney³ has shown that the measurements of SJ can be correlated with the data of Tinkham⁴ on paramagnetic resonance of Mn^{++} substitutional impurities in ZnF_2 . Much of our analysis will be based on Tinkham's work.

We shall also use data⁵ obtained by SJ from F^{19}

³ B. Bleaney, Phys. Rev. **104**, 1190 (1956).

⁴ M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 and 549 (1956).

⁵ V. Jaccarino and R. G. Shulman, Phys. Rev. **107**, 1196 (1957).

resonance in antiferromagnetic MnF_2 . From Tinkham's data, Bleaney predicted this resonance frequency at 0°K to be 179 Mc/sec, and from their paramagnetic data, SJ predicted 177 Mc/sec. The actual resonance was found near 160 Mc/sec. In Sec. III we present a consistent analysis of both paramagnetic and antiferromagnetic results which removes this discrepancy.

A theoretical interpretation of Tinkham's experiment has been given by Mukherji and Das.⁶ Their calculation is restricted to the isotropic effect. We discuss their results in Sec. VIII.

II. THE SHULMAN-JACCARINO EXPERIMENT

Following SJ we introduce a nuclear Hamiltonian for the k th F^{19} nucleus:

$$\mathcal{H}^k = -\gamma_N \hbar \mathbf{I}^k \cdot \mathbf{H}_0 + \sum_j \mathbf{I}^k \cdot \mathbf{A}^{jk} \cdot \mathbf{S}^j. \quad (3)$$

The first term is the usual Zeeman energy and the second term is an effective hyperfine coupling between the k th F^{19} nucleus and the j th manganese spin, summed over all near neighbors. In addition there will be terms from the manganese dipolar field as mentioned in Sec. I, and negligible contributions from nuclear dipole and quadrupole interactions. It will be the task of our theory to account for the effective hyperfine tensors \mathbf{A}^{jk} .

Since the manganese spin-relaxation time is very short compared with the nuclear resonance time, the nucleus will see the thermal average value $\langle \mathbf{S}^j \rangle_{\text{th}}$. This is related to the applied field and the paramagnetic susceptibility by

$$\langle \mathbf{S}^j \rangle_{\text{th}} = -H_0 \chi / N g \beta. \quad (4)$$

As emphasized by SJ, the simplicity of this equation depends upon the existence of an isotropic g tensor.

We may now write (3) in the form

$$\mathcal{H}^k = -\gamma_N \hbar \sum_\mu H_{0\mu} [I_\mu^k + \alpha \sum_j \sum_\nu I_\nu^k A_{\nu\mu}^{jk}], \quad (5)$$

where

$$\alpha = \chi / N g \beta \gamma_N \hbar,$$

and where the subscripts indicate vector and tensor components along appropriate orthogonal axes. We recall that the superscripts connect the k th F^{19} nucleus to its j th near-neighbor manganese spin. There are two nonequivalent fluorine sites in MnF_2 ; but since these differ only by a 90° rotation about the c axis, we need concern ourselves with the hyperfine interaction at only a single F^{19} nucleus. Thus we drop the index k and consider a nucleus situated as in Fig. 1. The x and z axes (the latter along c) are taken as shown in the figure; the y axis is normal to the page; these axes are principal axes of the hyperfine tensors.

For the nucleus shown in Fig. 1,

$$\mathcal{H} = -\gamma_N \hbar \sum_\mu H_{0\mu} I_\mu [1 + \alpha (A_\mu^I + A_\mu^{I'} + A_\mu^{II})]. \quad (6)$$

⁶ A. Mukherji and T. P. Das, Phys. Rev. **111**, 1479 (1958).

By reflection symmetry $A_\mu^I = A_\mu^{I'}$, but we preserve the distinction for the sake of clarity. The nucleus at the other type of site in MnF_2 will have an identical Hamiltonian with H_0 rotated by 90° about the z axis.

It is important to realize the difference between the environment seen by a manganese atom (Tinkham's problem⁴) and the environment of an F^{19} nucleus. If we consider the manganese at site II in Fig. 1, then it will see type II bonds to two neighbor fluorines along the x axis and type I bonds to four neighbor fluorines in the yz plane. The notation type I and type II is Tinkham's. We see that his A_μ^{II} will be identical to our A_μ^{II} , but that his A_μ^I will be related to our $A_\mu^{I'}$ and $A_\mu^{I''}$ by a 90° rotation about the z axis. Thus,

$$\begin{aligned} A_x^{I'} = A_x^{I''} = A_y^I; \quad A_y^{I'} = A_y^{I''} = A_x^I; \\ A_z^{I'} = A_z^{I''} = A_z^I. \end{aligned} \quad (7)$$

From application of Eq. (6) directly to their experiment, SJ were able to determine

$$\begin{aligned} 2A_z^I + A_z^{II} &= 47.0 \\ 2A_y^I + A_x^{II} &= 47.8 \quad \left\{ \begin{array}{l} 46.3 \\ 47.8 \end{array} \right\} \\ 2A_x^I + A_y^{II} &= 46.3 \quad \left\{ \begin{array}{l} 46.3 \\ 47.8 \end{array} \right\}. \end{aligned} \quad (8)$$

All values are with accuracies of ± 0.5 and are times 10^{-4} cm^{-1} . The numbers in braces are an alternate possible interpretation of the experiment.

To this set of parameters we shall add one obtained by the same authors⁵ from F^{19} resonance in antiferromagnetic MnF_2 . This parameter was determined by assuming complete sublattice magnetic saturation at 0°K . According to Kubo,⁷ however, spin-wave theory predicts that this structure should be short of complete saturation by $0.075/S$, or by 3% for $S = \frac{5}{2}$. We make this correction first to the dipole field, which we have calculated,² assuming saturation, to be 12 500 oe and which now becomes 12 120 oe at 0°K . This accounts for 48.56 Mc/sec of the measured resonance frequency and leaves us with

$$111.43 \text{ Mc/sec} = (2A_z^I - A_z^{II})(0.97S)c,$$

or

$$2A_z^I - A_z^{II} = (15.3 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}, \quad (9)$$

as compared with the value 14.6 ± 0.2 given by SJ.

In order to compare the four experimental values of

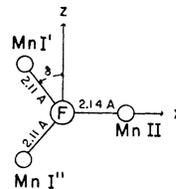


FIG. 1. Fluorine site in MnF_2 . The bond lengths are from Stout and Reed (see references 10 and 11).

⁷ R. Kubo, Phys. Rev. **87**, 568 (1952). A recent theory of J. C. Fisher, Bull. Am. Phys. Soc. **4**, 53 (1959), predicts only 1.3% short of saturation. Fisher's theory gives 14.9 for the numerical value in Eq. (9). The consequent changes in the values in Eq. (18) would be within the quoted errors.

(8) and (9) with theory we must return to the Hamiltonian in the form of Eq. (3) and relate this to contributions from fluorine $2s$ and $2p$ functions. But first we need a model of the fluorine orbitals.

III. THE INDEPENDENT-BONDING MODEL

If the covalent bonding tendencies are small, one may consider the fluorine as almost pure F^- . Then in a calculation involving any single $F-Mn$ bond we may think of that bond as a very small perturbation of the ionic configuration, and we may neglect any correlation effects among bonds as being of higher order in the perturbation. We simply add the independent effects of all the bonds. We shall call this the independent bonding model. Although they do not say so explicitly, both Tinkham and SJ analyze their data on the basis of this model; we shall rework their analysis with changes in emphasis and detail in order to clarify the argument and in order to correct some small, but important, numerical errors. In Sec. IV we consider the implications of a model in which the fluorine $2s$ and $2p$ orbitals hybridize and direct themselves towards the manganese neighbors.

We may choose p_x , p_y , and p_z functions corresponding to the axes of Fig. 1. However, since the matrix properties of these functions transform as simple vectors, we may equivalently analyze the p orbitals along and perpendicular to any bond we are considering. We make an independent analysis for each of the three types of bonds of Fig. 1. For each case we will call the p_v -orbital along the bond p_σ , the orbital along the y axis p_π , and the third and orthogonal orbital $p_{\pi'}$.

If we think of the hyperfine interaction of Eq. (3) as caused by an unbalance of fluorine electrons of up and down spins, we may write for the hyperfine expectation value:

$$A_\mu^j \langle I_\mu S_\mu^j \rangle = f_s \langle \mathcal{H}C_{2s} \rangle + \sum_\nu f_{p\nu} \langle \mathcal{H}C_{2p\nu} \rangle, \quad (10)$$

where f_s and $f_{p\nu}$ are the effective fractions of $2s$ and $2p_\nu$ electrons producing the net hyperfine interaction. The Hamiltonians of (10) are the standard atomic hyperfine interactions and have the expectation values for F^- ions:

$$\langle \mathcal{H}C_{2s} \rangle = A_{2s} \langle I_\mu S_\mu \rangle, \quad (11)$$

$$\langle \mathcal{H}C_{2p\nu} \rangle = A_{2p} \langle I_\mu S_\mu \rangle (3 \cos^2 \theta_{\mu,\nu} - 1),$$

where

$$A_{2s} = (8/3) \pi g \beta \gamma_N \hbar |\varphi_{2s}(0)|^2 = 1.57 \text{ cm}^{-1}, \quad (12)$$

$$A_{2p} = (2/5) g \beta \gamma_N \hbar \langle r^{-3} \rangle_{2p} = 0.044 \text{ cm}^{-1}.$$

Here $\theta_{\mu,\nu}$ is the angle between the bond direction of the p_ν orbital and the μ axis. The numerical values are those given by Moriya⁸ and are based on calculations by Hartree and by Barnes and Smith.⁹

We note that S_μ^j of Eq. (10) is the spin of an Mn^{++} ion, whereas S_μ of Eq. (11) is the spin of a single

unpaired fluorine electron. Therefore

$$\langle I_\mu S_\mu^j \rangle = 5 \langle I_\mu S_\mu \rangle;$$

and hence we may write

$$A_\mu^j = A_s^j + \sum_\nu A_{p\nu}^j (3 \cos^2 \theta_{\mu,\nu} - 1), \quad (13)$$

where

$$A_s^j = \frac{1}{5} f_s^j A_{2s}; \quad A_{p^j} = \frac{1}{5} f_{p^j} A_{2p}; \quad (14)$$

etc. for p_π and $p_{\pi'}$.

Noting that the three direction cosines in (13) sum in the square to one, we write

$$A_\mu^j = A_s^j + A_\sigma^j (3 \cos^2 \theta_{\mu,\sigma} - 1) + A_\pi^j (3 \cos^2 \theta_{\mu,\pi} - 1), \quad (15)$$

where A_s^j is shorthand for $(A_{p\sigma}^j - A_{p\pi'}^j)$ and A_π^j is shorthand for $(A_{p\pi}^j - A_{p\pi'}^j)$.

We now apply Eq. (15) to the bonds of Fig. 1, and we use Eq. (7). The result is

$$\begin{aligned} A_y^I &= A_s^I + (3 \sin^2 \delta - 1) A_\sigma^I - A_\pi^I, \\ A_x^I &= A_s^I - A_\sigma^I + 2 A_\pi^I, \\ A_z^I &= A_s^I + (3 \cos^2 \delta - 1) A_\sigma^I - A_\pi^I, \\ A_x^{II} &= A_s^{II} + 2 A_\sigma^{II} - A_\pi^{II}, \\ A_y^{II} &= A_s^{II} - A_\sigma^{II} + 2 A_\pi^{II}, \\ A_z^{II} &= A_s^{II} - A_\sigma^{II} - A_\pi^{II}. \end{aligned} \quad (16)$$

These equations contain six parameters on the right sides, whereas we have only four measurements in Eqs. (8) and (9). Strictly speaking, the independent-bonding model requires $A_{p\pi}^j = A_{p\pi'}^j$, and hence $A_\pi^j = 0$. This reduces (16) to four parameters. However, it also requires $A_y^{II} = A_z^{II}$, a relation in sharp disagreement with Tinkham's measurements (see next section). For reasons we shall give later, we do not believe that either $A_{p\pi}^j$ or $A_{p\pi'}^j$ is large enough to make a significant contribution, regardless of whether the two cancel or not; and therefore we shall drop A_π^j from (16). We may look on Tinkham's discrepancy as either an experimental error or as an indication that our theory is not quite complete and that A_π is taking the place of uncalculated effects which split A_y^{II} from A_z^{II} .

With A_π dropped, Eqs. (8), (9), and (16) lead to (all values in units of 10^{-4} cm^{-1})

$$\begin{aligned} A_s^I &= 15.4 \\ A_s^{II} &= 16.2 \\ A_\sigma^I &= 0.2 \\ A_\sigma^{II} &= 0.4 \end{aligned} \left\{ \begin{array}{l} 15.7 \\ 15.5 \\ -0.2 \\ -0.3 \end{array} \right\}. \quad (17)$$

Here we have used the value of $\cos^2 \delta = (\frac{1}{2}c/2.11)^2 = 0.615$, as appropriate for the MnF_2 lattice.^{10,11} The

¹⁰ We use the x-ray data of J. W. Stout and A. Reed, J. Am. Chem. Soc. **76**, 5279 (1954).

¹¹ Recent data of W. H. Baur, Acta Cryst. **11**, 488 (1958), gives the bond lengths as 2.13 Å for type I, 2.10 Å for type II. This makes $\cos^2 \delta = 0.604$, which is very near the value 0.603 used by SJ in their analysis. Small changes in $\cos^2 \delta$ (the value of which we regard as somewhat uncertain because of the conflicting data) fortunately do not lead to very significant changes in the results.

⁸ T. Moriya, Progr. Theoret. Phys. Japan **16**, 23 (1956).

⁹ R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

values in braces correspond to the braces of Eq. (8). Since all numbers are estimated to be in possible error by ± 0.3 , little significance can be attached to A_{σ}^I and A_{σ}^{II} . These should, however, be positive, and hence the nonbraced set is to be preferred. Using the values in Eqs. (14) and (12) we find

$$\begin{aligned} f_s^I &= (0.49 \pm 0.02) \times 10^{-2}, \\ f_s^{II} &= (0.52 \pm 0.02) \times 10^{-2}, \\ f_{p\sigma}^I - f_{p\pi}^I &= (0.2 \pm 0.3) \times 10^{-2}, \\ f_{p\sigma}^{II} - f_{p\pi}^{II} &= (0.4 \pm 0.3) \times 10^{-2}. \end{aligned} \quad (18)$$

These are the "measured values" of the effective fraction of fluorine electrons participating in the hyperfine interaction. In Secs. VIII and IX we compare these with theoretical values calculated from electronic overlap and hopping matrices.

The values (17) which are not in braces may be inserted into (16) to obtain (all in units of 10^{-4} cm^{-1})

$$\begin{aligned} A_y^I &= 15.4, & A_x^{II} &= 17.0, \\ A_x^I &= 15.2, & A_y^{II} &= 15.8, \\ A_z^I &= 15.6, & A_z^{II} &= 15.8. \end{aligned} \quad (19)$$

IV. THE HYBRIDIZED-ORBITALS MODEL

Let us assume that covalent tendencies are strong enough so that the appropriate fluorine orbitals are a hybridized set directed towards the manganese ions. We may form such an orthonormal set as follows:

$$\begin{aligned} \Psi_{I',I''} &= 2^{-\frac{1}{2}}[(1 - \tan^2\delta)^{\frac{1}{2}}\phi_s - (\tan\delta)\phi_x \pm \phi_z], \\ \Psi_{II} &= (\tan\delta)\phi_s + (1 - \tan^2\delta)^{\frac{1}{2}}\phi_x. \end{aligned} \quad (20)$$

The subscripts on Ψ indicate the manganese of Fig. 1 towards which the orbital is directed. The p_{π} function ϕ_y is nonhybridized.

We now assume these orbitals to be occupied by electrons of both up and down spins (with respect to H_0) with a slight fractional excess of down spin given by

Orbital	Fractional excess
$\Psi_{I',I''}$	a
Ψ_{II}	b
ϕ_y	c

Straightforward evaluation of the expectation value of the standard atomic hyperfine Hamiltonian then yields

$$\begin{aligned} 5A_y^I &= a[\frac{1}{2}(1-q)A_s + \frac{1}{2}(2q-1)A_p] - cA_p, \\ 5A_x^I &= a[\frac{1}{2}(1-q)A_s - \frac{1}{2}(1+q)A_p] + 2cA_p, \\ 5A_z^I &= a[\frac{1}{2}(1-q)A_s + \frac{1}{2}(2-q)A_p] - cA_p, \\ 5A_x^{II} &= b[qA_s + 2(1-q)A_p] - cA_p, \\ 5A_y^{II} &= b[qA_s - (1-q)A_p] + 2cA_p, \\ 5A_z^{II} &= b[qA_s - (1-q)A_p] - cA_p, \end{aligned} \quad (21)$$

with

$$q = \tan^2\delta.$$

A consistent fit (well within experimental errors) of Eqs. (8) and (9) can be made with

$$\begin{aligned} a &= (1.27 \pm 0.03) \times 10^{-2}, & b &= (1.63 \pm 0.03) \times 10^{-2}, \\ c &= (0.30 \pm 0.1) \times 10^{-2}. \end{aligned} \quad (22)$$

No fit can be made for the experimental parameters in braces. We should point out that the above fit is possible only if we allow $2A_x^I - A_z^{II} = -15.3 \times 10^{-4} \text{ cm}^{-1}$. However, the experiment cannot distinguish the sign of this parameter, since in the antiferromagnetic state half of the nuclei see a manganese spin environment just inverted with respect to that seen by the other half; thus two resonances will always be seen at \pm the absolute value of the effective internal z field, plus applied H_0 .

We may insert the values (22) back into (21) to obtain (all in units of 10^{-4} cm^{-1})

$$\begin{aligned} A_y^I &= 7.34, & A_x^{II} &= 32.83, \\ A_x^I &= 7.09, & A_y^{II} &= 32.01, \\ A_z^I &= 7.97, & A_z^{II} &= 32.21. \end{aligned} \quad (23)$$

Comparison of Eq. (23) with Eq. (19) reveals a marked difference between the two theories. The hybridized-orbitals model puts a major portion of the $2s$ function into Ψ_{II} , and therefore all A_{μ}^{II} are much larger than A_{μ}^I . (In order to obtain an equal amount of the $2s$ function in all the directed bonds we must have $\tan^2\delta = \frac{1}{3}$, i.e., trigonal symmetry.) On the other hand, as Eq. (19) shows, the independent-bonding model predicts all A_{μ}^I approximately the same magnitude as A_{μ}^{II} .

In the next section we discuss Tinkham's experiment, which gives direct evidence that Eq. (19) is very nearly correct for Mn-doped ZnF_2 . We are forced to conclude that the hybridized-orbitals model gives a very poor picture of the wave functions in MnF_2 or ZnF_2 . This is not surprising, since we know from other evidence that these crystals are highly ionic.

It would be interesting to try the hybridized-orbitals model on a reasonably covalent crystal, such as perhaps MnF_3 . Observations of nuclear resonance in this crystal have recently been reported, very briefly, by SJ.¹²

V. TINKHAM'S EXPERIMENT

In his paramagnetic resonance experiment on Mn^{++} -doped ZnF_2 , Tinkham obtains (all values in units of 10^{-4} cm^{-1}):

$$\begin{aligned} A_y^I &= 16.5 \pm 0.7, & A_y^{II} &= 14.6 \pm 1.2, \\ A_z^I &= 18.2 \pm 0.2, & A_z^{II} &= 12.5 \pm 0.2. \end{aligned} \quad (24)$$

The values include the direct dipolar interaction, of which more below. As pointed out in Sec. III, Tinkham noted that since $A_y^{II} \neq A_z^{II}$, it is necessary to retain A_{π} in Eq. (16). Since we have then six unknowns and

¹² R. G. Shulman and V. Jaccarino, Phys. Rev. **109**, 1084 (1957).

only four measurements, we must make some simplifications.^{12a}

For Tinkham's crystal, assuming that the presence of the slightly oversized Mn substitutional impurity does not distort the bond angles, we have^{10,13}

$$\cos^2\delta = (1.565/2.03)^2 = 0.594.$$

From the fourth and fifth of Eqs. (16) we obtain, from Tinkham's data, $A_{\pi}^{\text{II}} = 0.7$, and from the first and third of (16) we obtain $A_{\sigma}^{\text{I}} = 3.0$. If we now assume $A_{\pi}^{\text{I}} = A_{\pi}^{\text{II}}$ and $A_{\sigma}^{\text{I}} = A_{\sigma}^{\text{II}}$ we find (all values in units of 10^{-4} cm^{-1})

$$\begin{aligned} A_{\pi}^{\text{I}} = A_{\pi}^{\text{II}} = 0.7 \pm 0.4, & \quad A_s^{\text{I}} = 16.56 \pm 1.0, \\ A_{\sigma}^{\text{I}} = A_{\sigma}^{\text{II}} = 3.0 \pm 1.5, & \quad A_s^{\text{II}} = 16.2 \pm 1.5. \end{aligned} \quad (25)$$

As noted by Tinkham, his data include direct dipolar effects between the Mn spin and the F^{19} nucleus, and these vary with the same angular dependence as the A_{σ} term in Eq. (15). Thus the dipolar contributions may be thought of as contained in A_{σ} . The magnitude¹⁴ is $(g\beta\hbar\gamma_N/r^3) = 2.96 \times 10^{-4} \text{ cm}^{-1}$ for bond I, $2.92 \times 10^{-4} \text{ cm}^{-1}$ for bond II. Thus, without direct dipole:

$$A_{\sigma}^{\text{I}} = A_{\sigma}^{\text{II}} = 0 \pm 1.5. \quad (25')$$

We see that Tinkham's results are surprisingly close to those of SJ, Eq. (17). This close agreement was first noted by Bleaney,³ who actually used Tinkham's data to predict, with considerable accuracy, the F^{19} resonance frequency in antiferromagnetic MnF_2 .

If we correct (24) for the direct dipolar contribution, we obtain (all in units of 10^{-4} cm^{-1})

$$\begin{aligned} A_y^{\text{I}} = 15.9, & \quad A_y^{\text{II}} = 17.6, \\ A_z^{\text{I}} = 15.9, & \quad A_z^{\text{II}} = 15.4. \end{aligned} \quad (26)$$

^{12a} Note added in proof.—Recent work of Clogston, Gordon, Jaccarino, Peter, and Walker (private communication) demonstrates that the hyperfine tensors for Tinkham's case contain nondiagonal components. When these are incorporated into the analysis, the deduced values of A_{π} become insignificant.

¹³ Tinkham used the incorrect value $\cos^2\delta = 0.633$ in his analysis. This leads directly to $A_s^{\text{I}} = 1.2A_s^{\text{II}}$, which is an unusually rapid dependence on internuclear distance (the bond distances are 2.03 Å for type I, 2.04 Å for type II). Tinkham explained this dependence by including a large fraction of fluorine 3s and 3p functions into the bond. On the other hand, SJ analyzed their data assuming $A_s^{\text{I}} = A_s^{\text{II}}$ to be reasonable, and our analysis [Eq. (17)] gives $A_s^{\text{II}} = 1.05A_s^{\text{I}}$ (the bond distances in MnF_2 are 2.11 Å and 2.14 Å; note the greater difference than in ZnF_2). It is hard to reconcile these MnF_2 results with Tinkham's large 1.2 factor for ZnF_2 . However, as we show above, when our value of $\cos^2\delta$ is used we obtain $A_s^{\text{I}} = 1.02A_s^{\text{II}}$ from Tinkham's data—a reasonable result.

Recent data of W. H. Baur (see reference 11) give bond lengths in ZnF_2 as 2.04 Å for type I, 2.01 Å for type II, and hence $\cos^2\delta = 0.590$. This is a trivial change. It is interesting to note, however, that Stout and Reed find type I bonds shorter than type II in both MnF_2 and ZnF_2 whereas Baur finds type I bonds always longer. On the other hand, from SJ data we have, in MnF_2 $A_s^{\text{I}} > A_s^{\text{II}}$; and from Tinkham data, in ZnF_2 , $A_s^{\text{I}} < A_s^{\text{II}}$. Probably neither the x-ray nor the resonance experiments are sufficiently accurate to warrant any conclusions, however.

¹⁴ Tinkham uses a direct dipolar contribution one-half as large as ours. This, together with his value of $\cos^2\delta$, accounts for the difference between his and our final numerical results.

These should be compared with the SJ results, Eq. (19), based on the independent-bonding model. Comparison with Eq. (23) indicates the complete inapplicability of the hybridized-orbitals model.

VI. MANGANESE-FLUORINE WAVE FUNCTIONS

We take the ground state of MnF_2 as that of a perfect ionic crystal, which means that both ions have a closed-shell structure. Since, however, the charge clouds of both ions will overlap, this definition has a meaning only in the first approximation. For each ion we choose a set of Hartree-Fock wave functions which are computed for the ground state of a free ion. In the next approximation we take overlap of the wave functions into account.

We denote the Hartree-Fock orbitals of the $(2s)^2$ and $(2p)^6$ electrons in the F^- ion by

$$\phi_s \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \quad \phi_x \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \quad \phi_y \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \quad \phi_z \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

and the Hartree-Fock orbitals of the $(3d)^5$ electrons in the Mn^{++} ions by

$$(\psi_1, \psi_2, \psi_3, \psi_4, \psi_5)\alpha.$$

Consider the pair of F^- , Mn^{++} ions on the x axis of Fig. 1. Let ψ_1 have the angular factor $P_2^0(\cos\theta)$ where θ is with respect to the x axis, and call this $\psi_1 \equiv \psi_d$. The overlap integrals are defined by

$$S_s = \int \phi_s^*(\mathbf{r})\psi_d(\mathbf{r}-\mathbf{a})d\tau, \quad (27)$$

$$S_{\sigma} = \int \phi_x^*(\mathbf{r})\psi_d(\mathbf{r}-\mathbf{a})d\tau,$$

where \mathbf{a} is the distance between the centers of the two ions.

There will be no overlap between ϕ_s and the other ψ_i , which are of the form $Y_2^{\pm 1}$ and $Y_2^{\pm 2}$. The overlap S_{π} between $Y_2^{\pm 1}$ and the combinations $Y_1^{\pm 1}$ may be neglected since these charge clouds point parallel to each other. (It is for this reason that we dropped the A_{π} contribution in analyzing SJ data.)

Since from the experimental facts we expect the overlap integrals (27) to be rather small, we may restrict our attention to the 5-electron problem involving $\phi_s\alpha$, $\phi_s\beta$, $\phi_x\alpha$, $\phi_x\beta$, $\psi_d\alpha$ of a single Mn-F pair. This corresponds to the independent-bonding model of Sec. III.

The most important configurations are the ground-state configuration $(A) = (3d)^5(2s)^2(2p)^6$ and the two excited configurations involving electron transfer from fluorine to manganese $(B) = (3d)^6(2s)(2p)^6$ and $(C) = (3d)^6(2s)^2(2p)^5$. We note that only the fluorine electron of spin β can transfer. The relevant portion of the Slater determinants corresponding to these configura-

rations are

$$\begin{aligned}\Psi_A &= (5!)^{-\frac{1}{2}} |\phi_s\alpha(1), \phi_s\beta(2), \phi_x\alpha(3), \phi_x\beta(4), \psi_d\alpha(5)|; \\ \Psi_B &= (5!)^{-\frac{1}{2}} |\phi_s\alpha(1), \psi_d\beta(2), \phi_x\alpha(3), \phi_x\beta(4), \psi_d\alpha(5)|; \\ \Psi_C &= (5!)^{-\frac{1}{2}} |\phi_s\alpha(1), \phi_s\beta(2), \phi_x\alpha(3), \psi_d\beta(4), \psi_d\alpha(5)|.\end{aligned}\quad (28)$$

Because of manganese-fluorine overlap, these configurations are nonorthogonal. Neglecting terms higher than first order in the overlap, we have

$$\begin{aligned}\int \Psi_A^* \Psi_B d\tau &= \int \phi_s^*(\mathbf{r}) \psi_d(\mathbf{r}-\mathbf{a}) d\tau = S_s; \\ \int \Psi_A^* \Psi_C d\tau &= \int \phi_x^*(\mathbf{r}) \psi_d(\mathbf{r}-\mathbf{a}) d\tau = S_\sigma; \\ \int \Psi_B^* \Psi_C d\tau &= 0.\end{aligned}\quad (29)$$

The secular equation is

$$\begin{vmatrix} \mathcal{H}_{AA} - W & \mathcal{H}_{AB} - WS_s & \mathcal{H}_{AC} - WS_\sigma \\ \mathcal{H}_{BA} - WS_s & \mathcal{H}_{BB} - W & \mathcal{H}_{BC} \\ \mathcal{H}_{CA} - WS_\sigma & \mathcal{H}_{CB} & \mathcal{H}_{CC} - W \end{vmatrix} = 0.$$

To order S we may replace W in the off-diagonal elements by its zeroth-order value \mathcal{H}_{AA} and we may neglect \mathcal{H}_{BC} and \mathcal{H}_{CB} . Then standard perturbation theory yields as the first-order wave function

$$\Psi' = N[\Psi_A + \lambda_s \Psi_B + \lambda_\sigma \Psi_C], \quad (30)$$

with

$$\lambda_s = -T_s/\Delta_s; \quad \lambda_\sigma = -T_\sigma/\Delta_\sigma; \quad (31)$$

where

$$\begin{aligned}\Delta_s &= \mathcal{H}_{BB} - \mathcal{H}_{AA}; & \Delta_\sigma &= \mathcal{H}_{CC} - \mathcal{H}_{AA}; \\ T_s &= \mathcal{H}_{AB} - \mathcal{H}_{AA}S_s; & T_\sigma &= \mathcal{H}_{AC} - \mathcal{H}_{AA}S_\sigma.\end{aligned}\quad (32)$$

The constant N is for normalization. It is seen that the transfer integrals T include nonorthogonality effects.

The function (30) may be written as the single Slater determinant

$$\Psi' = N' |\phi_s\alpha(1), (\phi_s + \lambda_s\psi_d)\beta(2), \phi_x\alpha(3), (\phi_x + \lambda_\sigma\psi_d)\beta(4), \psi_d\alpha(5)|, \quad (33)$$

and therefore the mixture of three atomic-orbital configurations is equivalent to a single molecular-orbital configuration. One could, of course, have started with the function (33); the variational principle would then have yielded the solution (31) for the λ 's. It should be noted that (30) and (33) are equivalent only because the electron transfer in both excited atomic-orbital configurations is to the same orbital $\psi_d\beta$, and therefore the term in $\lambda_s\lambda_\sigma$ in (33) is zero.

VII. SPIN PROBABILITY DENSITIES

The nuclear resonance shift is produced by an unbalance of probability densities in the spin states α and β . To determine this unbalance, we must calculate

the probability density associated with our first-order wave function Ψ' . This is given by

$$\begin{aligned}\text{P.D.} &= \int |\Psi'(1, \dots, 5)|^2 d\tau_2 \cdots d\tau_5 \Big|_{r_1=r} \\ &+ \int |\Psi'(1, \dots, 5)|^2 d\tau_1 d\tau_3 \cdots d\tau_5 \Big|_{r_2=r} + \cdots \\ &+ \int |\Psi'(1, \dots, 5)|^2 d\tau_1 \cdots d\tau_4 \Big|_{r_5=r}.\end{aligned}\quad (34)$$

This expression is rather difficult to evaluate with the orbitals as given by Eq. (33). We may, however, simplify the problem tremendously by transformation of the orbitals of (33) into an orthogonal set. As discussed on p. 238 of Seitz,¹⁵ the Slater determinant is invariant to the orthogonalization process. This is because this process is equivalent to adding a constant multiple of the elements of one row of the determinant to the corresponding elements in another row, which procedure leaves the value of the determinant unchanged.

Let us assume we have transformed to an orthonormal set ϕ_i . Then (33) becomes

$$\Psi' = (5!)^{-\frac{1}{2}} |\phi_1(1), \phi_2(2), \phi_3(3), \phi_4(4), \phi_5(5)|, \quad (35)$$

and the probability density may be written simply as

$$\text{P.D.} = \sum_{i=1}^5 |\phi_i(\mathbf{r})|^2. \quad (36)$$

An orthonormal set may be obtained by the method of Löwdin¹⁶:

$$\begin{aligned}\phi_i &= \sum_j \phi_j (S^{-\frac{1}{2}})_{ji} \\ &= S_{ii}^{-\frac{1}{2}} [\phi_i - \frac{1}{2} \sum_j \phi_j S_{ji} + \frac{3}{8} \sum_{j,k} \phi_j S_{jk} S_{ki} - \cdots],\end{aligned}\quad (37)$$

where the ϕ_i are the original nonorthonormal orbitals of (33) and

$$S_{ji} = \int \phi_j^* \phi_i d\tau. \quad (38)$$

The integral includes a sum over spin states, that is, $S_{ji} = 0$ if the spins of ϕ_i and ϕ_j differ.

With this procedure, the orbitals become, to second order in λ and S ,

$$\begin{aligned}\phi_1 &= [\phi_s - \frac{1}{2} S_s \psi_d + \frac{3}{8} (S_s^2 \phi_s + S_s S_\sigma \phi_x)] \alpha, \\ \phi_2 &= (1 + \lambda_s^2 + 2\lambda_s S_s)^{-\frac{1}{2}} [\phi_s - \frac{1}{2} (\lambda_s S_s + \lambda_\sigma S_\sigma + \lambda_s \lambda_\sigma) \phi_x \\ &\quad + \lambda_s \psi_d] \beta, \\ \phi_3 &= [\phi_x - \frac{1}{2} S_\sigma \psi_d + \frac{3}{8} (S_\sigma^2 \phi_x + S_\sigma S_s \phi_s)] \alpha, \\ \phi_4 &= (1 + \lambda_\sigma^2 + 2\lambda_\sigma S_\sigma)^{-\frac{1}{2}} [\phi_x - \frac{1}{2} (\lambda_\sigma S_s + \lambda_\sigma S_\sigma + \lambda_s \lambda_\sigma) \phi_s \\ &\quad + \lambda_\sigma \psi_d] \beta, \\ \phi_5 &= [\psi_d - \frac{1}{2} S_s \phi_s - \frac{1}{2} S_\sigma \phi_x + \frac{3}{8} (S_s^2 + S_\sigma^2) \psi_d] \alpha.\end{aligned}\quad (39)$$

¹⁵ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

¹⁶ P.-O. Löwdin, *J. Chem. Phys.* **18**, 365 (1950).

The probability density of α spins is given by

$$\begin{aligned} (\text{P.D.})_\alpha &= |\phi_1|^2 + |\phi_3|^2 + |\phi_5|^2 \\ &= (1+S_s^2)\phi_s^2 + (1+S_\sigma^2)\phi_x^2 + (1+S_s^2+S_\sigma^2)\psi_d^2 \\ &\quad + 2\phi_s\phi_x S_s S_\sigma - 2\psi_d(S_s\phi_s + S_\sigma\phi_x), \end{aligned} \quad (40)$$

and similarly the probability density of β spins is given by

$$\begin{aligned} (\text{P.D.})_\beta &= (1-\lambda_s^2 - 2\lambda_s S_s)\phi_s^2 + (1+\lambda_\sigma^2 - 2\lambda_\sigma S_\sigma)\phi_x^2 \\ &\quad + (\lambda_s^2 + \lambda_\sigma^2)\psi_d^2 + 2\psi_d(\lambda_s\phi_s + \lambda_\sigma\phi_x) \\ &\quad - 2(\lambda_s S_s + \lambda_\sigma S_\sigma + \lambda_s\lambda_\sigma)\phi_s\phi_x. \end{aligned} \quad (41)$$

In these equations the expansion is to second order in λ and S . It is to be understood that ϕ_s and ϕ_x have argument (\mathbf{r}) whereas ψ_d has argument ($\mathbf{r}-\mathbf{a}$).

We shall be interested in the difference:

$$\begin{aligned} (\text{P.D.})_\alpha - (\text{P.D.})_\beta &= \left[(1 + \frac{1}{2}S_s^2 + \frac{1}{2}S_\sigma^2 - \frac{1}{2}\lambda_s^2 - \frac{1}{2}\lambda_\sigma^2)\psi_d \right. \\ &\quad \left. - (S_s + \lambda_s)\phi_s - (S_\sigma + \lambda_\sigma)\phi_x \right]^2. \end{aligned} \quad (42)$$

This may be thought of as the probability density of the augmented manganese function

$$\begin{aligned} \psi_d' &= (1 + \frac{1}{2}S_s^2 + \frac{1}{2}S_\sigma^2 - \frac{1}{2}\lambda_s^2 - \frac{1}{2}\lambda_\sigma^2)\psi_d \\ &\quad - (S_s + \lambda_s)\phi_s - (S_\sigma + \lambda_\sigma)\phi_x. \end{aligned} \quad (43)$$

This function is even correctly normalized through second order. This is the antibonding molecular orbital suggested by SJ in their Eq. (12), but we now see how it naturally arises from the total solution of the problem. If only S_s is taken account of, (43) reduces to

$$\psi_d' \approx (1 - S_s^2)^{-\frac{1}{2}}(\psi_d - S_s\phi_s). \quad (44)$$

This is the approximation of Mukherji and Das.⁶

VIII. CALCULATION OF THE ISOTROPIC SHIFT

The isotropic shift is given by the fractional probability charge evaluated at the fluorine nucleus (contact interaction). This is

$$f_s = \left[\frac{(\text{P.D.})_\alpha - (\text{P.D.})_\beta}{(\text{P.D.})_\beta} \right]_{\text{nucleus}} = (S_s + \lambda_s)^2. \quad (45)$$

Here we have neglected $\psi_d(-\mathbf{a})$ as negligible, that is, we assume that the charge density of the $3d$ function is very localized around the Mn nucleus.

We must now compute (45) and compare with the "measured value" of Eq. (18). From Sec. VI we have

$$\lambda_s = -T_s/\Delta_s = (\mathfrak{C}_{AA}S_s - \mathfrak{C}_{AB})/(\mathfrak{C}_{BB} - \mathfrak{C}_{AA}). \quad (46)$$

Terms of order S in \mathfrak{C}_{AA} may be dropped, and hence

$$\begin{aligned} \mathfrak{C}_{AA} &\approx 2(s|H|s) + (d|H|d) \\ &\quad + 2(sd|G|sd) + (ss|G|ss). \end{aligned} \quad (47)$$

Here, as usual¹⁷

$$H = (p_i^2/2m) - e^2 \sum_g (Z_g/r_{ig}), \quad G = e^2/r_{ij}.$$

¹⁷ For a more complete explanation of this notation, together with a discussion of the order of magnitude of the various integrals, see J. Yamashita and J. Kondo, Phys. Rev. **109**, 730 (1958).

To order S we have

$$\begin{aligned} \mathfrak{C}_{AB} &\approx (s|H|d) + (ss|G|sd) + (sd|G|dd) \\ &\quad + [(s|H|s) + (d|H|d) + (sd|G|sd)]S_s, \end{aligned} \quad (48)$$

and thus

$$\begin{aligned} T_s &\approx (s|H|d) + (ss|G|sd) + (sd|G|dd) \\ &\quad - [(sd|G|sd) + (s|H|s) + (ss|G|ss)]S_s. \end{aligned} \quad (49)$$

(a) Estimate of S_s

By using the Hartree-Fock wave functions of $\text{Mn}^{++} - (3d)$ and $\text{F}^- - (2s)$ we have estimated the value of S_s . The computation is straightforward and the result is

$$S_s \approx 0.05. \quad (50)$$

The same result was obtained independently by Mukherji and Das.⁶ These authors calculate the overlap appropriate to the two Mn-F distances of Tinkham's experiment. They obtain a theoretical ratio $A_s^{\text{I}}/A_s^{\text{II}} = 1.05$. (However, although they use a molecular orbital picture, they do not consider the λ_s contribution.) Their theoretical ratio should be compared with Tinkham's 1.20 and with our correction to Tinkham, 1.02 (see reference 13). The distances used by Mukherji and Das are those of Stout and Reed; use of the data of Baur would lead to a theoretical ratio less than 1.

(b) Estimate of λ_s

By a rather rough calculation we have estimated the value of the first four terms in (49) to be ~ -0.01 atomic unit (a.u.). For the fifth term we have used the value of $(s|H|s)$ computed by Hartree, that is, -1.0765 a.u., and we have calculated the sixth term by using the Hartree-Fock wave functions of the $2s$ electron. The total result is

$$T_s \sim -0.015 \text{ a.u.} \approx -0.4 \text{ ev.} \quad (51)$$

This number is difficult to estimate with precision since the last three terms of (49) tend to cancel the first three terms. However, the order of magnitude should be correct.

Next let us estimate Δ_s . The principal contributions are

(a) the orbital energy of a $2s$ electron in the F^- ion, which is calculated by Hartree as -1.0765 a.u., or about -29 ev;

(b) the orbital energy of a P_2^0 -type electron in the $(3d)^6$ configuration of Mn^+ , which we estimate from the spectrum data (Kaiser's table) as about -10 ev;

(c) the change in the electrostatic energy due to the transfer. This will be equal to the energy created in an MnF_2 crystal by placing a negative electron at a Mn^{++} site and a positive electronic charge at a F^- site, or (neglecting charge overlap and polarization effects) equal to

$$-eV_{\text{Mn}} + eV_{\text{F}} - (e^2/a). \quad (52)$$

Here V_{Mn} and V_{F} are the crystalline electrostatic potentials at the Mn and F sites, respectively, and a is the smallest Mn-F separation. We may relate this expression to the Madelung energy per molecule,¹⁸

$$-(\alpha/a)e^2 = \frac{1}{2}[V_{\text{Mn}}(2e) + 2V_{\text{F}}(-e)], \quad (53)$$

where α is the Madelung constant ($=4.816$). The electrostatic energy-change due to transfer is thus

$$(4.816-1)(e^2/a) = 0.95 \text{ a.u.} \approx 26 \text{ ev.}$$

The value of Δ_s is $(29-10+26)=45$ ev in the first approximation. The effect of lattice polarization around the excess charge will of course reduce this energy. We know from the work of Mott and Littleton however that this polarization energy is only of the order of several electron volts, so it is doubtful if Δ_s can be smaller than ~ 35 ev. Thus we can hardly expect a larger value than

$$\lambda_s \sim 0.4/35 = 0.01. \quad (54)$$

We note that λ is positive, which corresponds to a reasonable molecular orbital in Eq. (43).

(c) Estimate of Isotropic Shift

The isotropic shift is now given by

$$f_s = (S_s + \lambda_s)^2 = (0.06)^2 = 0.36 \times 10^{-2}, \quad (55)$$

which is to be compared to the experimental value 0.50×10^{-2} of Eq. (18). At the present state of the development the reason for the discrepancy is not clear, although we can imagine the following possible causes: (1) The theoretical value of S_s is not accurate, because the wave functions of the free ions should be modified in the crystal. In particular, the crystalline field may deform the F^- ion; and since this field consists of electrostatic field, exchange effects, and overlap effects, the degree of deformation will depend on the spin configuration of the surrounding Mn ions. (2) The theoretical value of T_s is not accurate for similar reasons. (3) The estimate of Δ_s is in error. (4) There are other causes of the shift.

IX. CALCULATION OF THE ANISOTROPIC SHIFT

The net anisotropic hyperfine interaction will be proportional to

$$\int (1-3 \cos^2\theta)r^{-3}[(\text{P.D.})_\alpha - (\text{P.D.})_\beta]d\tau, \quad (56)$$

where θ is the angle between \mathbf{r} and the axis of quantization. On substitution of Eq. (42) into the above, it is seen that the contribution from ψ_d^2 is simply the dipolar field, at the F nucleus, of a Y_2^0 electron centered about

the neighbor Mn (multiplied by a very small correction). When this is added to the dipolar fields of the other four Mn $3d$ electrons, one has the dipolar field of a spherical cloud at a point essentially outside the cloud. This is the same as the dipolar field from an equivalent spin at the Mn nucleus, plus higher poles which may be neglected. This dipolar field has already been included in the dipolar lattice sum.

The contribution from the ϕ_s^2 and the $\phi_s\phi_x$ terms will integrate to zero.

The contribution from the $\psi_d\phi_s$ and $\psi_d\phi_x$ cross terms may be estimated as follows. We assume that the overlap region is concentrated along the Mn-F axis at the fluorine ionic radius r_I . Then we obtain, approximately

$$\begin{aligned} & (1-3 \cos^2\theta_I)r_I^{-3} \left[-2(S_s + \lambda_s) \int \psi_d^* \phi_s d\tau \right. \\ & \left. - 2(S_\sigma + \lambda_\sigma) \int \psi_d^* \phi_x d\tau \right] \\ & \approx -2(1-3 \cos^2\theta_I)r_I^{-3} [S_s(S_s + \lambda_s) + S_\sigma(S_\sigma + \lambda_\sigma)], \quad (57) \end{aligned}$$

where θ_I is the angle between the axis of quantization and the Mn-F axis.

Finally we have the contribution to (56) from the ϕ_x^2 term:

$$\begin{aligned} & (S_\sigma + \lambda_\sigma)^2 \int (1-3 \cos^2\theta)r^{-3} |\phi_x|^2 d\tau \\ & = (S_\sigma + \lambda_\sigma)^2 (1-3 \cos^2\theta_I) (2/5) \langle r^{-3} \rangle_{2p}. \quad (58) \end{aligned}$$

The anisotropic shift is given by the sum of (57) and (58) divided by

$$\int (1-3 \cos^2\theta)r^{-3} (\text{P.D.})_\beta d\tau.$$

Thus:

$$f_{p\sigma} = (S_\sigma + \lambda_\sigma)^2 - 0.045 [S_s(S_s + \lambda_s) + S_\sigma(S_\sigma + \lambda_\sigma)], \quad (59)$$

where the numerical value is obtained from $\langle r^{-3} \rangle_{2p}$ as given by Barnes and Smith⁹ and r_I as approximated by the Pauling radius of F^- .

By using the Hartree-Fock wave functions, we have computed¹⁹

$$S_\sigma = 0.060. \quad (60)$$

By methods similar to those of Sec. VIII we have estimated $T_\sigma \approx -0.4$ ev. In the case of the $2p_\sigma$ -electron the orbital energy in the F^- ion is only about -4 or -5 ev, so that Δ_σ becomes $\sim 10-15$ ev. Hence

$$\lambda_\sigma \sim 0.4/10 = 0.04, \quad (61)$$

¹⁸ See M. Born and M. Goepfert-Mayer, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, part 2, page 707. The definition of the Madelung constant given on p. 77 of reference 15 does not correspond, for the rutile structure, to the value of the Madelung constant given in that book.

¹⁹ A preprint version of our work which was distributed in October, 1958, gave $S_\sigma = 0.045$. A subsequent calculation by W. Marshall yielded a higher value. We wish to thank Dr. Marshall for calling our attention to this discrepancy, which led to discovery of the omission of an important term in our original calculation.

or perhaps less. Finally

$$f_{p\sigma} \sim 1 \times 10^{-2}, \quad (62)$$

or perhaps less. The $\psi_a\phi_x$ and $\psi_a\phi_s$ cross terms in (59) make a very small contribution.

This is to be compared to the experimental values of Eq. (18). It is seen to be much too large, although the uncertainty in the experimental values makes definite conclusion unwise. The discrepancy could be caused by (1) a non-negligible value of $f_{p\pi}$; (2) underestimate of the size of the cross terms.

We note that, regardless of the signs of S or λ , Eqs. (55) and (59) predict a paramagnetic shift, i.e., ΔH

positive. However, the ψ_1 electron must exist in the transition metal ion for the theory to apply. In the case of CrF_3 , where this electron is expected to be absent, the nuclear resonance is found to be unshifted.²⁰

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²⁰ Jaccarino, Shulman, and Stout, Phys. Rev. **106**, 602 (1957).

Anomalous Skin Effect in Bismuth*†

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High-frequency (23.5-kMc/sec) surface resistance measurements have been made on plane surfaces of single-crystal bismuth at 2°K as a function of orientation. It has been ascertained that extreme anomalous skin effect conditions prevail, allowing details of the Fermi surface to be deduced from Pippard's theory. In Shoenberg's model of the electron band, components of the inverse effective-mass tensor divided by the Fermi energy are found to be $\alpha_1/E_e=9.10$, $\alpha_2/E_e=0.088$, $\alpha_3/E_e=4.7$, and $\alpha_4/E_e=0.38$ (in units of $10^3/\text{ev}$). These results are in essential agreement with values obtained from de Haas-van Alphen experiments and cyclotron resonance. The number of ellipses is definitely established to be six and the number of electrons found to be $N=5.5 \times 10^{17}/\text{cm}^3$. The parameters for the two hole ellipsoids are found to be $\beta_1/E_h=\beta_2/E_h=1.5$ and $\beta_3/E_h=0.12$. Assuming Shoenberg's value $E_e=0.0177$ ev, we calculate $E_h=0.00112$ ev from specific heat data. It is also found that the reflection of carriers from the surface of the sample is predominantly specular in contrast to diffuse reflection found in other metals.

1. INTRODUCTION

IT has been shown^{1,2} that measurements of the high-frequency surface resistance of pure single-crystal metals can yield valuable information about the Fermi surface when so-called extreme anomalous conditions are achieved. This requires that the mean free path l be much greater than the skin depth δ , and that $\omega\tau$ be small enough to prevent relaxation effects, where ω is the frequency and τ the relaxation time.

For a plane surface, the surface resistance will have the form

$$R=R_x \cos^2\theta + R_y \sin^2\theta, \quad (1)$$

where x and y are principal axes of the surface, and θ

the angle between the current direction and the x axis. Pippard,¹ assuming that only those electrons traveling nearly parallel to the surface are effective in absorbing energy, derives the expression

$$R_x = b \frac{\sqrt{3} \left[\frac{\pi \omega^2 \hbar^3}{2 [e^2 c^4 \int |\rho_y| dy] \right]^{\frac{1}{2}}}, \quad (2)$$

where ρ_y is the radius of curvature of the Fermi surface in a plane normal to the y axis at the point where the normal to the Fermi surface is parallel to the surface of the metal. The quantities ρ_y and y are expressed in units of momentum. The integration must include summing over all sheets of the Fermi surface when it is not simply connected. A similar expression holds for R_y . The constant b is equal to 8/9 for specular reflection of electrons from the surface of the metal and equal to 1 for diffuse reflection. The choice of b for the interpretation of the present experiment will be discussed in Sec. 5. It will be noted that R is independent of the relaxation time and depends only on the geometrical shape of the Fermi surface. It is further evident that a deduction of the Fermi surface from the measured

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¹ A. B. Pippard, Proc. Roy. Soc. (London) **A224**, 273 (1954).

² E. H. Sondheimer, Proc. Roy. Soc. (London) **A224**, 260 (1954).