

concentration has not been evaluated at successive stages. While no additional EPR spectra which might correspond to the intermediate forms were seen, it is doubtful that these would be sharp enough for detection, in view of the severe axial fields possible at the ion site in the intermediate forms.

It is beyond the scope of this paper to determine in detail the rate constants and free energies for the reactions connecting the two different environments giving spectra I and II. We can only say that the behavior with thermal cycling suggests that II is stable

at higher temperatures, including the range 700 to 1050°C, but is metastable at lower temperatures, as shown by its disappearance at 380°K.

Note added in manuscript. Our conclusion that oxidation of CaF₂:Mn²⁺ leads to containment of the manganese ions in disoriented regions of CaO in the crystal is consistent with the following reports on work done with powders: P. H. Kasai, *J. Phys. Chem.* **66**, 674 (1962); R. L. Hickok, J. A. Parodi, and W. G. Segelken, *J. Phys. Chem.* **66**, 2715 (1962); J. A. Parodi, *J. Electrochem. Soc.* **114**, 370 (1967).

PHYSICAL REVIEW

VOLUME 163, NUMBER 2

10 NOVEMBER 1967

Overlap Contribution to the Isomer Shift of Iron Compounds*

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(Received 12 June 1967)

The electron density $\Psi^2(0)$ at the iron nucleus in oxides is calculated as a function of the Fe-O distance, by taking into account the overlap of the inner shells of iron with the oxygen $2p$ wave functions. The calculation shows the importance of the intershell terms, which effectively reduce the overlap-induced electron density. By comparing these results with the high-pressure isomer-shift measurements of divalent iron in CoO, the relative change of the ⁵⁷Fe nuclear radius is found to be less than -4.0×10^{-4} . The overlap effect provides an important amplification mechanism for the contribution of $4s$ bonding to $\Psi^2(0)$. On the basis of this mechanism, large increases in $\Psi^2(0)$ observed on going from Fe²⁺ to Fe³⁺ salts can be explained by a reasonable increase in the amount of $4s$ bonding.

I. INTRODUCTION

IT is well known that the Mössbauer isomer shift (I.S.) depends primarily on the difference in the electron charge density at the nucleus between the absorber and emitter. In the nonrelativistic approximation, this dependence can be written as follows¹:

$$\text{I.S.} = \frac{2}{5}\pi Ze^2(R_{\text{exc}}^2 - R_{\text{gd}}^2)[\Psi_A^2(0) - \Psi_E^2(0)], \quad (1)$$

where R_{exc} and R_{gd} are the nuclear-charge radii of the first excited and ground states, and $\Psi_A^2(0)$ and $\Psi_E^2(0)$ are the s -electron densities at the nucleus for the absorber and emitter, respectively. Equation (1) has been used by Walker *et al.*¹ to calibrate the isomer shift of ⁵⁷Fe. Their procedure was based on the observation that the isomer-shift difference between various ionic ferrous and ferric absorbers, relative to a common source, has a constant value of about 0.9 mm/sec. By assuming that $\Psi^2(0)$ in these salts is correctly

given by the computations of Watson² for $3d^5$ and $3d^6$ free ions, Walker *et al.*¹ determined the relative change of the nuclear charge radius to be

$$\Delta R/R = (R_{\text{exc}} - R_{\text{gd}})/R_{\text{gd}} = -1.8 \times 10^{-3}. \quad (2)$$

Watson's² results predict a change in $\Psi^2(0)$ from 118.813×10^2 to $118.796 \times 10^2 a_0^{-3}$ on going from Fe³⁺ to Fe²⁺. The small difference between the latter values ($=1.76 a_0^{-3}$) is almost entirely due to the shielding of the $3s$ wave function by the additional $3d$ electron. The contribution of the $3s$ wave function to $\Psi^2(0)$ is $140 a_0^{-3}$, and it is obvious that a small deviation from this Hartree-Fock value, due to correlation, could lead to a considerable uncertainty in the calibration of the ⁵⁷Fe isomer shift. Another source of error comes from the effect of the $3d$ and $4s$ covalent bonding, which is very difficult to estimate with sufficient accuracy. It is interesting to note that smaller values of $\Delta R/R$ have been predicted by Goldanskii³ and Danon⁴ on the basis

* Supported in part by the National Science Foundation and the Office of Naval Research, Grant No. NONR 233(88).

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¹L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

²R. E. Watson, Solid State and Molecular Theory Group, Technical Report No. 12, Massachusetts Institute of Technology, 1959 (unpublished).

³V. I. Goldanskii, in *Proceedings of the Dubna Conference on the Mössbauer Effect* (Translated by Consultants Bureau Enterprises, Inc., New York, New York, 1963), pp. 17-19.

⁴J. Danon, in *Applications of the Mössbauer Effect* (International Atomic Energy Agency, Vienna, Austria, 1966), Series No. 50, p. 89.

of chemical arguments. Therefore, the problem of calibrating the ^{57}Fe isomer shift must be regarded as still open.

In the present paper, we propose a calibration procedure which is based on the changes of the ^{57}Fe isomer shift with interionic distance. Recently, high-pressure Mössbauer measurements have been performed in a few ionic salts.⁵ The observed increases in $\Psi^2(0)$ with pressure have been attributed⁵ to a spreading out of the $3d$ electrons towards ligand accompanied by a decrease of the amount of $3d$ - $3s$ shielding. Though this spreading seems to occur for antibonding electrons,⁶ the bonding electrons are responsible for a net increase of the amount of $3d$ charge with increasing pressure, producing a decrease in $\Psi^2(0)$.

Several years ago, Marshall⁷ pointed out that the overlap of the iron inner shells with ligand wave functions produces a significant change in $\Psi^2(0)$. The mechanism for this change is called the overlap distortion. It is a direct consequence of the Pauli exclusion principle which forces the electrons to keep out of the overlap region enhancing $\Psi^2(0)$ at the nucleus. Because of the dependence of overlaps on the interionic distance, this enhancement exhibits a pressure dependence of the required sign. Using Watson's^{2,8} wave functions for Fe^{3+} and O^{2-} , we calculate the rate of change of $\Psi^2(0)$ with the Fe-O distance. The results indicate that overlap distortion provides the dominant mechanisms for the volume and pressure-dependent isomer shift in compounds with negligible $4s$ bonding (divalent iron salts). An interesting feature of this calculation arises from the presence of negative intershell terms ($1s$, $2s$ and $2s$, $3s$) which markedly reduce the overlap contribution to $\Psi^2(0)$. The same "cancellation" effect was observed in the previous study⁹ of "supertransferred" hyperfine interaction.

In view of the above mentioned difficulties with the isomer-shift calibration based on different valencies of

⁵ C. J. Coston, R. Ingalls, and H. G. Drickamer, *J. Appl. Phys.* **37**, 1400 (1966); and R. Ingalls, C. J. Coston, G. De Pasquali, H. G. Drickamer, and J. J. Pinajian, *J. Chem. Phys.* **45**, 1057 (1966).

⁶ The idea of a spreading out of the $3d$ orbitals with pressure is supported by the experimentally observed decrease of the Racah parameters with increasing pressure [H. G. Drickamer, *Solid State Phys.* **17**, 1 (1965)]. This is consistent with the conjecture that decreased interatomic distance implies greater covalent mixing. First, increase of the latter is accompanied by an increase in the amount of $3d$ electrons accommodated in the bonding orbitals. These electrons act to expand the radial $3d$ orbitals on account of Coulomb shielding. Second, the normalization constant in the antibonding orbitals decreases with increasing covalency, leading to a decrease of the Racah parameters. The assumption of the increase of covalency with decreased interionic distance is also supported by the fact that the Racah parameters decrease with decreasing electron affinity of the ligands.

⁷ W. Marshall, in *Proceedings of the Second International Conference on the Mössbauer Effect*, edited by A. H. Schoen and D. M. J. Compton (John Wiley & Sons, Inc., New York, 1962), p. 263.

⁸ R. E. Watson, *Phys. Rev.* **111**, 1108 (1958).

⁹ Nai Li Huang, R. Orbach, and E. Šimánek, *Phys. Rev. Letters* **17**, 134 (1966).

iron, it seems advantageous to apply the overlap distortion effect to the ^{57}Fe isomer-shift calibration. When the calculated changes in $\Psi^2(0)$ with distance are compared with the high-pressure isomer-shift measurement⁵ of divalent iron in CoO, the value of $\Delta R/R$ is found to be -4.0×10^{-4} which is not far from the value -5×10^{-4} suggested by Goldanskii.³

In trivalent iron salts, one has to take into account the effects of $4s$ bonding. Danon⁴ suggested a configuration, $3d^5 4s^0$,³² for trivalent iron in typically ionic salts. In order to calculate the combined effect of $4s$ bonding and inner shells on $\Psi^2(0)$, we incorporate the $4s$ admixture into the orthogonalized ligand orbital. The expression for $\Psi^2(0)$ then contains positive ($1s$, $4s$), ($3s$, $4s$) and negative ($2s$, $4s$) cross-terms, which result in a positive term linear in the $4s$ admixture. The latter is responsible for a strong enhancement of the contribution to $\Psi^2(0)$ from $4s$ bonding. This enhancement is important for explaining the large increase in $\Psi^2(0)$ observed on going from Fe^{2+} to Fe^{3+} salts. The experimental isomer shifts for the latter are consistent with our new calibration ($\Delta R/R \cong -4 \times 10^{-4}$) if we assume that the iron configurations are $3d^6$ and $3d^5 4s^0$ in divalent and trivalent salts, respectively.

Obviously, $4s$ bonding produces stronger changes in $\Psi^2(0)$ than the same amount of $3d$ bonding. Hence, we expect that the net effect of $3d$ and $4s$ bonding will be an increase of $\Psi^2(0)$ with pressure. In the analysis of the pressure-dependent isomer shift of ^{57}Fe in CoO we have completely neglected $3d$ and $4s$ bonding. Consequently, the value of $\Delta R/R (-4.0 \times 10^{-4})$, deduced from this analysis represents an upper limit to the actual value.

II. OVERLAP CONTRIBUTION TO $\Psi^2(0)$

In the interpretation of the ^{57}Fe isomer shift, Walker *et al.*¹ have identified $\Psi^2(0)$ in ionic salts with the free-ion density:

$$\Psi^2(0) = 2 \sum_{n=1}^3 \phi_{ns}^2(0), \quad (3)$$

where ϕ_{ns} are the $1s$, $2s$, and $3s$ wave functions for free iron ions calculated by Watson.² In an ionic solid, these wave functions overlap with ligand orbitals leading to the overlap-distortion effect. Using the Heitler-London model, these overlaps can be accounted for by orthogonalizing the ligand orbitals to the ϕ_{ns} functions.

As a specific example, we consider the Fe^{3+} ion surrounded by an oxygen octahedron. Then the overlap distortion is almost entirely due to the six equivalent $2p_\sigma$ oxygen orbitals. The $\langle \phi_{ns} | 2p_\sigma \rangle$ overlaps can be accounted for by constructing an orthogonalized ligand orbital

$$\chi' = N \left(\chi - \sum_{n=1}^3 S_{ns} \phi_{ns} \right), \quad (4)$$

where χ is a symmetric combination of the $2p_\sigma$ orbitals, designated as p_i , S_{ns} is the group overlap integral

$$S_{ns} = \langle \phi_{ns} | \chi \rangle, \quad (5)$$

and

$$N = \left(1 - \sum_{n=1}^3 S_{ns}^2\right)^{-1/2}. \quad (6)$$

The properly normalized ligand molecular orbital χ , has a form

$$\chi = \left[6 \left(1 + \sum_{j=2}^6 \langle p_1 | p_j \rangle\right)\right]^{-1/2} (p_1^+ p_2^+ \cdots p_6). \quad (7)$$

The ionic configuration consisting of orthogonalized orbitals with A_{1g} symmetry has the wave function

$$\Psi = (8!)^{-1/2} \{ \phi_{1s}^+, \phi_{1s}^-, \phi_{2s}^+, \phi_{2s}^-, \phi_{3s}^+, \phi_{3s}^-, \chi'^+, \chi'^- \}, \quad (8)$$

where (+) and (-) denote the up and down spin, respectively, and the curly brackets indicate a determinantal wave function. The total electron charge density due to Ψ is a sum of the individual one-electron contributions. Neglecting small terms containing the amplitude of χ at the position of iron nucleus, the result is

$$\Psi^2(0) = 2 \sum_{n=1}^3 \phi_{ns}^2(0) + \delta\Psi^2(0), \quad (9)$$

where

$$\delta\Psi^2(0) = 2 \left[\sum_{n=1}^3 S_{ns}^2 \phi_{ns}^2(0) + 2 \sum_{n,m=1}^3 S_{ns} S_{ms} \phi_{ns}(0) \phi_{ms}(0) \right]. \quad (10)$$

$\delta\Psi^2(0)$ is the electron charge density at the iron nucleus induced by the overlap effect. Using (7), the group overlaps S_{ns} can be expressed in terms of the

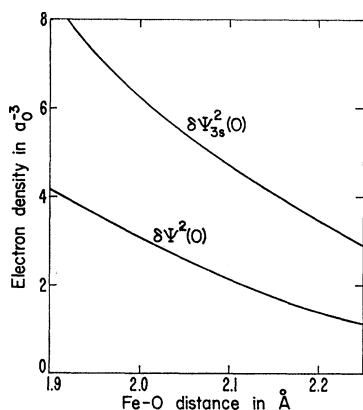


FIG. 1. The s -electron densities induced by the overlap effect at the nucleus of the Fe^{3+} ion in an oxygen octahedron. $\delta\Psi^2(0)$ is the overlap contribution (11) of the $1s$, $2s$, and $3s$ shells, $\delta\Psi_{3s}^2(0)$ is due to the $3s$ shell only. Both electron densities are plotted as a function of the Fe-O distance. The calculation of (11) is based on values of S_{ns} calculated for various Fe-O distances by Huang (Ref. 11) (see Table I).

TABLE I. Overlap integrals $s_{ns} = \langle \phi_{ns} | 2p \rangle$ calculated (Ref. 11) with the ϕ_{ns} wave functions (Ref. 2) for Fe^{3+} , and the $2p$ wave function (Ref. 8) for O^{2-} . a is the Fe-O distance in Å.

a	S_{1s}	S_{2s}	S_{3s}
1.94	0.00314	0.02337	0.11216
2.00	0.00286	0.02136	0.10309
2.10	0.00241	0.01815	0.08842
2.16	0.00217	0.01647	0.08063
2.22	0.00196	0.01496	0.07354

atomic overlaps $s_{ns} = \langle \phi_{ns} | 2p \rangle$, and $\delta\Psi^2(0)$ then becomes

$$\delta\Psi^2(0) = 2 \left[\sum_{n=1}^3 \frac{6}{1+R'} S_{ns}^2 \phi_{ns}^2(0) + 2 \sum_{n,m=1}^3 \frac{6}{1+R'} S_{ns} S_{ms} \phi_{ns}(0) \phi_{ms}(0) \right], \quad (11)$$

where

$$R' = \sum_{j=2}^6 \langle p_1 | p_j \rangle.$$

If we neglect the ligand-ligand overlap ($R'=0$) and put $S_{1s}=S_{2s}=0$, expression (11) goes over into the formula previously derived by Flygare and Hafemeister.¹⁰ They calculated the overlap distortion of the outermost $5s$ shell of I^- in alkali halides. It turns out that in the case of iron, the terms in (10) containing S_{1s} and S_{2s} strongly influence the resulting value of $\delta\Psi^2(0)$. Numerical calculations show that the negative cross product ($2s$, $3s$) nearly cancels the diagonal $3s$ contribution. This situation is similar to that previously encountered in the calculation of the overlap contribution to the supertransferred hyperfine interaction.⁹

The electron charge density (11) exhibits a characteristic dependence on the Fe-O distance (denoted as a) which can be evaluated if we assume that the one-electron wave functions ϕ_{ns} and $2p$ remain independent of a . The overlaps $\langle \phi_{ns} | 2p \rangle$ have been calculated by Huang¹¹ with the use of Watson's Fe^{3+} wave functions² and O^{2-} solutions⁸ in a stabilizing potential well due to the $+2e$ spherical charge (see Table I). We use the same $2p$ functions to calculate the ligand-ligand correction and find R' to be about 0.4. With these data we calculate $\delta\Psi^2(0)$ for various distances around $a=2$ Å, with the result shown in Fig. 1. In order to demonstrate the above-mentioned cancellation effect, we also plot the electron charge density $\delta\Psi_{3s}^2(0)$ which arises from (11) by putting $S_{1s}=S_{2s}=0$. We notice a drastic decrease in $\delta\Psi^2(0)$ and its slope, caused mainly by the negative ($2s$, $3s$) cross product. It is possible that a similar cancellation effect is present between $5s$ and $4s$ shells of I^- in alkali halides.

¹⁰ W. H. Flygare and D. W. Hafemeister, *J. Chem. Phys.* **43**, 789 (1965).

¹¹ Nai Li Huang (private communication).

III. ENHANCEMENT OF THE 4s EFFECT

So far, we have considered the electron charge density arising from a purely ionic configuration with overlapping orbitals. In trivalent iron salts, covalent 3d and 4s bonding become important. Covalent 3d bonding in transition-metal oxides is believed to be due to the $2p \rightarrow 3d$ transfer which increases the number of 3d-electrons on the metal ion. Consequently, the amount of 3d-3s shielding increases, decreasing $\Psi^2(0)$. On the other hand, 4s bonding causes an increase in $\Psi^2(0)$ on account of the direct contribution $\phi_{4s}^2(0)$ of the 4s electrons. In the presence of the inner-shell overlap effect described above, 4s bonding contributes to $\Psi^2(0)$ by additional cross products, which effectively enhance the direct contribution. By recalling that 4s bonding arises from the $\chi \rightarrow 4s$ transfer, we can incorporate the 4s admixture parameter a_{4s} into the ligand orbital χ' , thus forming a bonding orbital

$$\chi'' = N(\chi - \sum_{n=1}^3 S_{ns}\phi_{ns} + a_{4s}\phi_{4s}). \quad (12)$$

Constructing a determinantal wave function from ϕ_{ns} and χ'' as before, we find the total electron charge density at the iron nucleus to be

$$\begin{aligned} \Psi^2(0) = & 2 \sum_{n=1}^3 \phi_{ns}^2(0) \\ & + 2 \left[\sum_{n=1}^3 S_{ns}^2 \phi_{ns}^2(0) + 2 \sum_{n,m=1}^3 S_{ns} S_{ms} \phi_{ns}(0) \phi_{ms}(0) \right. \\ & \left. + a_{4s}^2 \phi_{4s}^2(0) - 2 \sum_{n=1}^3 a_{4s} S_{ns} \phi_{ns}(0) \phi_{4s}(0) \right]. \quad (13) \end{aligned}$$

The modified 4s contribution to $\Psi^2(0)$ can thus be written as follows:

$$\delta\Psi_{4s}^2(0) = 2 \left[a_{4s}^2 \phi_{4s}^2(0) - 2 \sum_{n=1}^3 a_{4s} S_{ns} \phi_{ns}(0) \phi_{4s}(0) \right]. \quad (14)$$

The first term on the right-hand side of (14) is the direct 4s contribution, the second one is a sum of cross products between the 4s, and the inner shells. According to the estimates of Walker *et al.*,¹ $\phi_{4s}^2(0)$ in trivalent iron is found to be $7.5 a_0^{-3}$. By considering a typical Fe-O distance $a = 2 \text{ \AA}$, we evaluate the overlaps in (14) and obtain (see Appendix)

$$\delta\Psi_{4s}^2(0) = 15a_{4s}^2 + 13a_{4s}. \quad (15)$$

The second term, linear in a_{4s} , is responsible for the enhancement of the 4s contribution to the electron charge density. For the configuration $3d^5 4s^0$,³² $a_{4s}^2 = 0.16$ and $\delta\Psi_{4s}^2(0) = 7.6a_0^{-3}$, which should be compared with the direct 4s contribution equal to $2.4a_0^{-3}$. The amplification effect is more important for small values of a_{4s} (small direct contribution). It is to be noted, that the same amount of 3d bonding (changing $3d^5$ to

$3d^{5.3}$) causes $\Psi^2(0)$ to decrease by about $0.6a_0^{-3}$ only. Hence, we can expect that 4s bonding has a dominating effect on $\Psi^2(0)$, so that the net effect of 3d and 4s bonding is an increase in $\Psi^2(0)$.

It should be emphasized that (15) is not suitable for calculating $\delta\Psi_{4s}^2(0)$ as a function of internuclear distance. The problem is that both a_{4s} and $\phi_{4s}(0)$ vary with internuclear distance in a complicated manner. Equation (15) mainly demonstrates the overlap enhancement for "fixed" parameters a_{4s} and $\phi_{4s}(0)$.

IV. CALIBRATION OF THE ^{57}Fe ISOMER SHIFT

Coston *et al.*⁵ find that the isomer shift of divalent iron in CoO changes from -1.16 mm/sec at atmospheric pressure to -1.08 mm/sec at 250 kbar, relative to a stainless-steel absorber. X-ray diffraction measurements¹² show that the relative reduction of the Co-O distance at 250 kbar is $a/a_0 = 0.965$. We now estimate the change in $\Psi^2(0)$ produced by this reduction on account of the overlap effect. By recalling that the inner-shell orbitals change very little on going from Fe^{3+} to Fe^{2+} , we can use here the calculations of $\delta\Psi^2(0)$ made for Fe^{3+} ion. According to Fig. 1, the reduction $a/a_0 = 0.965$ causes an increase in the overlap-induced density $\delta\Psi^2(0)$ by about $0.7a_0^{-3}$. In addition to this, the decrease of a is accompanied by an increase of 3d and 4s covalent bonding.⁶ The effects of the changing covalency on $\Psi^2(0)$ cannot be estimated reliably and we will neglect them in analyzing the above data. We expect that the amplified 4s effect is stronger than the counteracting 3d effect. Hence, by neglecting the covalency effects, we actually underestimate the increase in $\Psi^2(0)$ with pressure. By introducing the overlap-induced increase ($= 0.7a_0^{-3}$) and the difference in the experimental⁵ isomer shifts ($= 0.08$ mm/sec) into (1), we determine the relative change of the nuclear-charge radius to be $\Delta R/R = -4 \times 10^{-4}$. This is a much smaller change than that predicted by Walker *et al.*¹ but it is close to the value $\Delta R/R = -5 \times 10^{-4}$, suggested by Goldanskii.³ By omitting the covalency effects, we are actually calculating the upper limit of the magnitude of $\Delta R/R$.

If we assume that the new calibration ($\Delta R/R \cong -4 \times 10^{-4}$) is correct, there remains to be explained the large increase in $\Psi^2(0)$ observed on going from Fe^{2+} to Fe^{3+} salts. The relative isomer shift between the latter is found to be about 0.9 mm/sec, which corresponds to an increase in $\Psi^2(0)$ of about $8a_0^{-3}$. By taking into account the overlap effect and the fact that the Fe-O distance in trivalent salts is about 7% shorter than that in divalent salts, we obtain from Fig. 1 an increase in $\delta\Psi^2(0)$ by about $1.2a_0^{-3}$ only. Danon⁴ suggested that the most ionic trivalent iron salts have a configuration $3d^5 4s^0$,³² corresponding to a 4s bonding

¹² H. G. Drickamer, R. W. Lynch, R. L. Clendenen, and E. A. Perez-Albuern, *Solid State Phys.* **19**, 135 (1966).

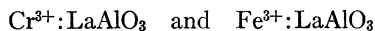
admixture $a_{4s}^2=0.16$. According to Eq. (15) this admixture causes an increase in $\delta\Psi^2(0)$ of about $7.6a_0^{-3}$. In addition to this, we get an increase of $\Psi^2(0)$ in Fe^{3+} due to the change in the $3d$ occupation. The latter gives a contribution to $\Psi^2(0)$ around $1a_0^{-3}$, and its exact value depends on the amount of $2p \rightarrow 3d$ transfer. By taking all these contributions into account we can obtain a total required increase of $8a_0^{-3}$ if we assume that the iron configurations in divalent and trivalent salts are $3d^6$ and $3d^54s^{0.2}$, respectively. Hence, as a result of the enhancement of the $4s$ contribution, the large increase in $\Psi^2(0)$ can be explained by a reasonable amount of $4s$ bonding.

Trivalent iron in garnets and spinels is distributed over the tetrahedral (A) and octahedral (B) sites. In spinels, the relative isomer shifts $[\text{I.S.}(A)-\text{I.S.}(B)]$ are scattered around -0.1 mm/sec. The larger electron density at the A site is usually attributed to an increase in the amount of $4s$ bonding. With our calibration of the ^{57}Fe isomer shift ($\Delta R/R \cong -4 \times 10^{-4}$), the relative shift -0.1 mm/sec corresponds to an increase in $\Psi^2(0)$ of about $0.9a_0^{-3}$, which is equivalent to the direct effect of 12% of the $4s$ electron. By taking into account the overlap effect and the fact that the Fe-O distance is about 5% shorter in the A site than in the B site, we find from (14) that this increase ($0.9a_0^{-3}$) can be accounted for by assuming configurations $3d^54s^{0.2}$ and $3d^54s^{0.32}$ for B and A site, respectively. This calculation shows that $S_{ns}(\text{oct}) > S_{ns}(\text{tetra})$, provided the same $2p$ wave functions are used for both sites. Consequently, the terms in (14) which are linear in a_{4s} have almost the same magnitude for both sites, so that the resulting increase in $\Psi^2(0)$ arises mainly from the direct $4s$ effect.

V. DISCUSSION

Before we suggest the adoption of a new value for $\Delta R/R$, we have to consider the uncertainties involved in our calibration procedure. The most serious one is the lack of accuracy in calculating the overlap-distortion effect.

This problem has already been discussed in connection with cation-cation hyperfine interaction¹³ in trivalent iron salts. It has been suggested¹⁴ that the repulsive potential of the closed shells surrounding a given O^{2-} ion may reduce the overlaps $\langle \phi_{ns} | 2p \rangle$ calculated from Watson's⁸ wave functions. On the other hand, investigation¹⁵ of cation-cation hyperfine interaction in



indicates a need for an oxygen $2p$ wave function which is more extended than Watson's solution.

Obviously, reliable values of $\langle \phi_{ns} | 2p \rangle$ must be based on wave functions obtained variationally¹⁶ by minimizing the total energy of the crystal. In view of the difficulties with the wave function of O^{2-} , it would be advantageous to study the pressure dependence of the isomer shift in fluorides, in which the F^- wave functions are believed to coincide with the well known free-ion Hartree-Fock solutions.¹⁷

ACKNOWLEDGMENTS

We thank Professor R. Mössbauer, Professor R. Orbach, Dr. Nai Li Huang, and Dr. M. Tachiki for valuable discussions, and Professor H. G. Drickamer for helpful correspondence and valuable comments on the original manuscript.

APPENDIX

A brief description is presented of the steps which turn Eq. (14) into (15). The group overlap integrals S_{ns} are calculated from the atomic overlap integrals $s_{ns} = \langle \phi_{ns} | 2p \rangle$ using the relation

$$S_{ns} = [6/(1+R')]^{1/2} s_{ns}, \quad (\text{A1})$$

which follows from (7). Calculations of Huang¹¹ give $s_{1s} = 0.00286$, $s_{2s} = 0.02136$, and $s_{3s} = 0.10309$ for the Fe^{3+} - O^{2-} distance equal to 2 Å. We take $|\phi_{1s}(0)| = 73.30$, $|\phi_{2s}(0)| = 22.21$, and $|\phi_{3s}(0)| = 8.31$ a.u., as given by the computations of Watson² for Fe^{3+} ion. Using these values, the estimate¹ $|\phi_{4s}(0)| = 2.74$ a.u., and $R' = 0.4$, the cross terms in (14) come out as

$$-4S_{1s}\phi_{1s}(0)\phi_{4s}(0) = 4.7$$

$$-4S_{2s}\phi_{2s}(0)\phi_{4s}(0) = -10.7$$

$$-4S_{3s}\phi_{3s}(0)\phi_{4s}(0) = 19.4$$

$$\text{Coefficient of } a_{4s} = 13.4 [a_0^{-3}]. \quad (\text{A2})$$

We see that the dominant contribution to the coefficient of a_{4s} is due to the positive ($3s, 4s$) term. As in the pure overlap effect (see Sec. II), the negative ($2s, 4s$) term diminishes the result. The signs of the contributions in (A2) are determined by the number of nodes of the ϕ_{ns} wave functions (see Refs. 9, 14, and 15).

¹³ J. J. Van Loef, *Physica* **32**, 2102 (1966).

¹⁴ E. Šimánek, Nai Li Huang, and R. Orbach, *J. Appl. Phys.* **38**, 1072 (1967).

¹⁵ D. R. Taylor, J. Owen, and B. M. Wanklyn (to be published).

¹⁶ J. Yamashita and M. Kojima, *J. Phys. Soc. Japan* **7**, 261 (1952).

¹⁷ The calculations for fluorides will appear in a subsequent paper.