

### Calibration of the Fe<sup>57</sup> Isomer Shift\*

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The *s*-electron density at the iron nucleus in KFeF<sub>3</sub> is calculated as a function of the Fe-F distance, using the Heitler-London model and the Hartree-Fock ionic wave functions. By comparing the calculated "overlap-induced" *s*-electron density with the hydrostatic pressure isomer shift measurements in KFeF<sub>3</sub>, the relative change of the Fe<sup>57</sup> nuclear radius is found to be  $-5.2 \times 10^{-4}$ , which is to be compared with the value  $-1.8 \times 10^{-3}$  derived previously by Walker *et al.*

IN the nonrelativistic approximation, the isomer shift  $\Delta E_{IS}$  as measured in Mössbauer experiments is related to the *s*-electron density at nucleus by means of the expression<sup>1</sup>

$$\Delta E_{IS} = (4\pi Z e^2 / 5) R^2 (\Delta R / R) \{ \psi_A^2(0) - \psi_B^2(0) \}, \quad (1)$$

where  $\psi_A^2(0)$  and  $\psi_B^2(0)$  are the total *s*-electron densities at nucleus for absorber and emitter, respectively, and  $\Delta R / R$ , the calibration constant, is given by

$$\Delta R / R = (R_{\text{exo}} - R_{\text{gd}}) / R_{\text{gd}}, \quad (2)$$

where  $R_{\text{exo}}$  and  $R_{\text{gd}}$  are the nuclear-charge radii of the first excited and ground states, respectively, and  $R = \frac{1}{2}(R_{\text{exo}} + R_{\text{gd}}) \approx R_{\text{gd}}$ . Several years ago, Walker *et al.*<sup>1</sup> determined the calibration constant  $\Delta R / R$  for Fe<sup>57</sup> using the isomer-shift difference between ferrous and ferric absorbers. By assuming that  $\psi^2(0)$  in these salts is correctly given by the free-ion Hartree-Fock computations of Watson,<sup>2</sup> they found  $\Delta R / R = -1.8 \times 10^{-3}$ .

A new method has recently been suggested<sup>3</sup> for determining  $\Delta R / R$  in Fe<sup>57</sup>, which is based on comparison of the high-pressure isomer-shift measurements<sup>4</sup> in ionic salts with the calculation of the overlap-induced charge density  $\delta\psi^2(0)$  as a function of interionic distance. This method has been applied<sup>3</sup> to the case of CoO, yielding an upper bound of  $|\Delta R / R|$  equal to  $4 \times 10^{-4}$ . The calculation of  $\psi^2(0)$  involves overlap integrals between inner *s* shells of iron and the *2p* wave functions of O<sup>2-</sup>. In view of the fact that the O<sup>2-</sup> ion does not exist in a free state, there are difficulties in obtaining a realistic form of the *2p* wave function of O<sup>2-</sup> ion in a crystal. The previous calculation<sup>3</sup> of  $\psi^2(0)$  in CoO was based on Watson's<sup>5</sup> solutions for *2p* wave function of O<sup>2-</sup> imbedded in a stabilizing potential of spherical  $+2e$  charge. Since the *2p* wave function is

very spread out, it is sensitive to the particular crystal environment and consequently large errors can be committed in calculating overlap integrals with the use of Watson's solutions.<sup>5</sup> In addition to this, the measurements of the isomer shift versus pressure in CoO are not accurate enough to form a good basis for the calculation.

Recently, Champion, Vaughan, and Drickamer<sup>6</sup> reported new measurements of high-pressure isomer shifts in fluorides, such as FeF<sub>2</sub> and FKFeF<sub>3</sub>. It is the purpose of this paper to report on a determination of  $\Delta R / R$  in Fe<sup>57</sup>, based on the data for KFeF<sub>3</sub>. In fluorides, we believe that the F<sup>-</sup> ion wave functions may be taken to be the free-ion Hartree-Fock wave functions in a good approximation, and thus the above-mentioned uncertainty in the calculation of the overlap integrals can be reduced. Also the experimental data for fluorides<sup>6</sup> are an order of magnitude more accurate than those for oxides.<sup>5</sup> Consequently, a more reliable value for  $\Delta R / R$  can be expected from the use of fluoride data.

For an octahedral environment of Fe<sup>2+</sup> in KFeF<sub>3</sub>, we can use the expression for  $\delta\psi^2(0)$  derived in Ref. 3 on the basis of the Heitler-London model which takes into account the overlaps between the inner *s* shells of iron and the *2p* shells of the anions. This overlap-induced *s*-electron density is

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

where

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

is a sum of ligand-ligand overlaps (running over the octahedron corners) and  $s_{ns} = \langle \phi_{ns} | p \rangle$  is the overlap integral between the inner *ns* orbital  $\phi_{ns}$  of iron and the *2p<sub>σ</sub>* orbital of the F<sup>-</sup> ion. We have evaluated the integrals  $s_{ns}$  for various Fe-F distances using the  $\phi_{ns}$  orbitals of Fe<sup>2+</sup>, given by Watson,<sup>2</sup> and the Hartree-

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

<sup>3</sup> E. Šimánek and Z. Šroubek, Phys. Rev. **163**, 275 (1967)

<sup>4</sup> C. J. Coston, R. Ingalls, and H. G. Drickamer, J. Appl. Phys. **37**, 1400 (1966).

<sup>5</sup> R. E. Watson, Phys. Rev. **111**, 1100 (1958).

<sup>6</sup> A. R. Champion, R. W. Vaughan, and H. G. Drickamer (to be published).

Fock<sup>7</sup>  $2p$  wave function of  $F^-$ . These values for  $s_{ns}$  are calculated by using the modified version of the Switendick-Corbato MIDIAT program.<sup>8</sup> The results are summarized in Table I. The ligand-ligand correction  $R'$  is estimated, using the overlap tables,<sup>9</sup> to be about 0.18 for the equilibrium interionic distances in  $KFeF_3$ . The dependence of  $\delta\psi^2(0)$  on the Fe-F distance calculated from (3) is plotted in Fig. 1.

To calculate the increase of  $\delta\psi^2(0)$  with pressure, we need the bulk compressibility of  $KFeF_3$ . The latter can be estimated by comparison with a similar crystal of  $KMgF_3$  where the elastic moduli  $C_{11}$  and  $C_{12}$  have been determined from ultrasonic measurements.<sup>10</sup> In this way we find that the low-pressure bulk compressibility  $K=3/(C_{11}+2C_{12})$  of  $KMgF_3$  is about 2.2 times larger than that of  $MgO$ . Assuming the same compressibility for  $KFeF_3$  and using the recent  $p$ - $V$  data for  $MgO$  by Drickamer,<sup>11</sup> we obtain a decrease of the equilibrium Fe-F distance (2.06 Å) of about 1.8% on increasing the hydrostatic pressure from 0 to 50 kbar. For this decrease, Fig. 1 predicts an increase of  $\delta\psi^2(0)$  by  $0.20a_0^{-3}$ . For the same pressure increase, the experimental data<sup>6</sup> in  $KFeF_3$  indicate a decrease of the isomer shift by 0.03 mm/sec. Putting these values into (1), obtains  $\Delta R/R = -5.2 \times 10^{-4}$ , which is about  $\frac{1}{4}$  of the value reported by Walker *et al.*,<sup>1</sup> but close to the value  $-5 \times 10^{-4}$  suggested by Goldanskii.<sup>12</sup>

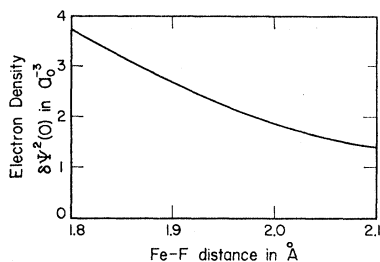


FIG. 1. The overlap-induced  $s$ -electron density  $\delta\psi^2(0)$  at the of the  $Fe^{2+}$  ion in a fluorine octahedron calculated as a function of the Fe-F distance from (3).

<sup>7</sup> According to R. E. Watson, the radial part of the  $2p$  wave function of  $F^-$  ion is

$$R_{2p}(r) = r \{ 11.4933 \exp(-4.6968r) + 4.9377 \exp(-2.4322r) + 0.8533 \exp(-1.5722r) + 0.2216 \exp(-0.9261r) \}$$

(private communication with Dr. Nai Li Huang).

<sup>8</sup> A. C. Switendick and F. J. Corbato, Massachusetts Institute of Technology Solid State and Molecular Theory Group, Quarterly Progress Report No. 34, 1959 (unpublished).

<sup>9</sup> R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.* **17**, 1248 (1949).

<sup>10</sup> H. M. Rosenberg and J. K. Wigmore, *Phys. Letters* **24A**, 317 (1967).

<sup>11</sup> H. G. Drickamer, R. W. Lynch, R. L. Clendensen, and E. A. Perez-Albuerno, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 19, p. 135.

<sup>12</sup> V. I. Goldanskii, in *Proceedings of the Dubna Conference on the Mössbauer Effect* (Consultants Bureau Enterprises, Inc., New York, 1963), pp. 17-19.

TABLE I. The overlap integrals  $s_{ns} = \langle \phi_{ns} | p \rangle$  between the inner  $s$  orbitals of  $Fe^{2+}$  and the  $2p$  orbital of the  $F^-$  ion.

$d$ (Å)	$s_{1s}$	$s_{2s}$	$s_{3s}$
1.78	0.002827	0.020986	0.107270
1.82	0.002624	0.019529	0.100116
1.86	0.002444	0.018228	0.093688
1.90	0.002272	0.016988	0.087490
1.92	0.002194	0.016430	0.084703
1.94	0.002118	0.015876	0.081918
1.96	0.002042	0.015327	0.079140
1.98	0.001971	0.014815	0.076550
2.00	0.001904	0.014336	0.074132
2.02	0.001839	0.013861	0.071717
2.04	0.001775	0.013404	0.069385
$d_{\text{equil}} = 2.06$	0.001710	0.012928	0.066954
2.10	0.001598	0.012117	0.062804

Though the ionic fluorides such as  $KFeF_3$  are believed to be fairly well described by the Heitler-London model, one can expect that  $\delta\psi^2(0)$  may actually deviate from (3) because of the following effects. First, the outermost atomic orbitals ( $3d$  and  $4s$  of  $Fe^{2+}$  and  $2p$  of  $F^-$ ) may change with pressure. Secondly, there may be a pressure-dependent electron transfer from the ligands to the  $3d$  and  $4s$  iron states. The latter covalency effects have been discussed in Ref. 3, and it has been shown that the  $3d$  covalency effect is overcome by the  $4s$  contribution amplified by the admixture of the inner  $s$  shells. The net covalency effect is then an increase of  $\delta\psi^2(0)$  with pressure. Hence, by using the purely ionic formula (3), we are actually underestimating the calculated increase of  $\delta\psi^2(0)$  with pressure. Consequently, the above deduced value of  $5.2 \times 10^{-4}$  represents an upper bound to  $|\Delta R/R|$  for  $Fe^{57}$ . The covalency effects are believed to be larger in oxides than in fluorides, and thus we expect a smaller value of  $|\Delta R/R|$  from the Heitler-London interpretation of the oxide data. The fact that the previously<sup>3</sup> deduced value for  $|\Delta R/R|$  using  $CoO$  data is only slightly smaller indicates that Watson's  $2p$  wave function<sup>5</sup> for  $O^{2-}$  is not largely overestimating the overlap effect (due to overdiffuseness) in  $CoO$  as previously<sup>13</sup> suspected for trivalent iron oxides.

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<sup>13</sup> E. Šimánek, Nai Li Huang, and R. Orbach, *J. Appl. Phys.* **38**, 1072 (1967).