Isomer shift and charge density in FeAl and the ^{57}Fe isomer shift

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The isomer shift of FeAl with respect to Fe metal is measured to be $+0.272 \pm 0.015$ mm sec^{-1}. The difference in the electronic charge density at the Fe site in Fe metal and FeAl is calculated from the band structures of Fe and FeAl to be $-0.698 a_0^{-3}$. These data are used in conjunction with recent published band-structure, atomic-structure, and molecular-orbital calculations to determine the isomer-shift calibration constant for ^{57}Fe to be $-0.206 \pm 8\%$ a_0^3 mm sec^{-1}.

I. INTRODUCTION

The isomer shift of ^{57}Fe compounds has been extensively studied since 1961 when Walker et al.[1] first proposed an electron-configuration diagram which yielded a value of -0.51 a_0^3 mm sec^{-1} for the isomer-shift calibration constant. A survey by Duff[2] showed that from 1961 until 1973 the calculated value of α which appeared in the literature ranged from -0.11 to -0.51 a_0^3 mm sec^{-1}. These researches included measurements on a variety of compounds coordinated with a variety of calculations. Calculations included wave functions generated by the use of Slater-type orbitals,[3-5] Gaussian orbitals,[2,6] and band calculations.[7,8] Most of the measurements and calculations were made for compounds which showed a positive isomer shift with respect to Fe metal. Most of the charge-density calculations for these compounds were based on atomic orbitals referred to Fe free atoms. In 1975, Mielczarek and Winfree[8] measured the negative isomer shift for TiFe with respect to Fe metal. That measurement in conjunction with the charge density obtained from the TiFe band calculation of Papaconstantopoulos,[9] and calculations by Duff on FeF$_2$ and K$_3$FeF$_6$ yielded a value of α equal to -0.19 a_0^3 mm sec^{-1}.

In the present work we report on a measurement of the isomer shift of FeAl which is positive with respect to Fe metal. Both the TiFe and FeAl data are analyzed utilizing the band-structure results of Ref. 9 for TiFe and of Nagel et al.[10] for FeAl. These data are then used with the recent work of Reschke et al.,[11] Micklitz et al.,[12] and Nieuwpoort et al.,[13] which are based on atomic-structure and molecular-orbital calculations to extract a value for α.

II. THEORY

A brief outline of the theory of the isomer shift is given in our previous work[8] and a more complete discussion is given in the many published review books on the Mössbauer effect.[14] Only the major definitions of this theory will be reiterated here. The isomer shift is the shift in nuclear transition energy reflecting a perturbation of the nuclear energy levels due to electrostatic interactions between the nucleus and its electronic environment. Equation 1 gives the isomer shift energy difference expressed in terms of the Doppler shifted velocity Δv. This equation represents the measurement of two different absorbers referred to the same source:

$$\Delta v = (\tfrac{2}{3}\pi)e^2 Z c E_\gamma^{-1} S'(Z)[\Delta\rho(0)]\delta\langle r^2\rangle. \tag{1}$$

Here Δv is expressed in cm sec^{-1}, c is the velocity of light, E_γ is the energy of the nuclear transition, and the electronic charge e is expressed in electrostatic units. Z is the atomic number, $\delta\langle r^2\rangle$ is the difference in mean-square nuclear charge radius between the isomers and $\Delta\rho(0)$ is the difference in electronic charge density at the nucleus for the two absorbers. $S'(Z)$ is a relativistic correction to the wave function. For the 14.4-keV transition in ^{57}Fe Eq. (1) becomes

$$\Delta v = 14.3\Delta\rho(0)S'(Z)\delta\langle r^2\rangle, \tag{2}$$

where $\Delta\rho$ is expressed as charge density per Bohr volume (a_0^3) and Δv is in mm sec^{-1}. Calculations of $\delta\langle r^2\rangle$ and $S'(Z)$ would thus yield a value for α, the calibration constant, where

$$\Delta v = \alpha\Delta\rho(0). \tag{3}$$

The value of $S'(Z)$ was first calculated by Shirley[15] to be 1.29 and a recent calculation by Mallow et al.[16] agrees with this value to within 1%.

III. EXPERIMENTAL MEASUREMENTS

The FeAl sample measured in this experiment was prepared by Metals Research Ltd.[17] Weighed

pure metals were outgassed and then induction re-melting was performed to promote homogeneity. A sample 2 mm thick was cut using a high-speed water-cooled tungsten carbide wheel. The surface used in the backscattering measurement was polished by standard metallographic techniques. Electron probe microanalysis, powder diffraction measurements, and optical photography were performed by Nagel[18] in order to determine the composition and structure of the sample. These measurements yielded an upper limit of 3% for deviation from the stoichiometric composition of the sample.

The experimental system and computer program used were the same as in our previous work.[8] The method of calculating the channel number for the peak position and correction for systematic error between first- and second-half velocity wave form data accumulation is also described in Ref. 8. The only differences between the previous work[8] and this work is that back scattered resonant emission of the 6-keV γ ray associated with the 14.4-keV transition was observed and the Co-Pd source was approximately 25 mCi. Six alternating runs of this solid FeAl sample and an Fe calibrating foil were made with both source and absorber at room temperature. The time of data accumulation for each run averaged three days. The results of these runs give a value of +0.272 ± 0.015 mm sec^{-1} for the isomer shift of FeAl with respect to Fe metal. The error quoted is the largest deviation from the average of the runs. Previous measurements of the FeAl isomer shift are reported by Frankel et al.[19] and Wertheim et al.[20] on powdered samples. However, the primary impetus for both of these works was not a measurement of the isomer shift but an investigation of the existence of a magnetic moment. Neither work discusses the calibration procedure or quotes an error. The Frankel et al. measurement was made with respect to sodium ferrocyanide, the Wertheim et al. measurement with respect to ^{57}Co-Pd. Both measurements fall within 15% of ours. Figure 1 shows the backscattering spectrum from one of our runs (No. 106). The linewidth (half-width at half-maximum) for this run was 30 channels, i.e., 0.20 mm sec^{-1}.

IV. CHARGE-DENSITY CALCULATION

Crystal potentials generated by self-consistent band-structure calibrations were used to calculate the charge densities of s character at the Fe nucleus in FeAl, Fe, and TiFe.

We have used for FeAl the potential of Nagel et al.[10] for pure Fe the crystal charge densities of Wakoh and Yamashita[7] (WY) and for TiFe the potential of Papaconstantopoulos.[9] Both of the metal-compound calculations were done using the $X\alpha$ treatment of exchange, while the WY calculation used an exchange potential which accounts for the spin orientation of the electrons. The calculation proceeds as follows. The self-consistent crystal potential is used to solve the Schrödinger equation by the augmented plane wave (APW) method for 10 $\vec{k}$ points in the $\frac{1}{48}$th of the simple cubic Brillouin zone for TiFe and FeAl and for 14 $\vec{k}$ points in the $\frac{1}{48}$th of the bcc Brillouin zone for Fe. This calculation yields the crystal wave functions of the valence band corresponding to the Fe atomic levels $3d$ and $4s$. Those wave functions are used to construct the corresponding angular momentum components of the charge density.
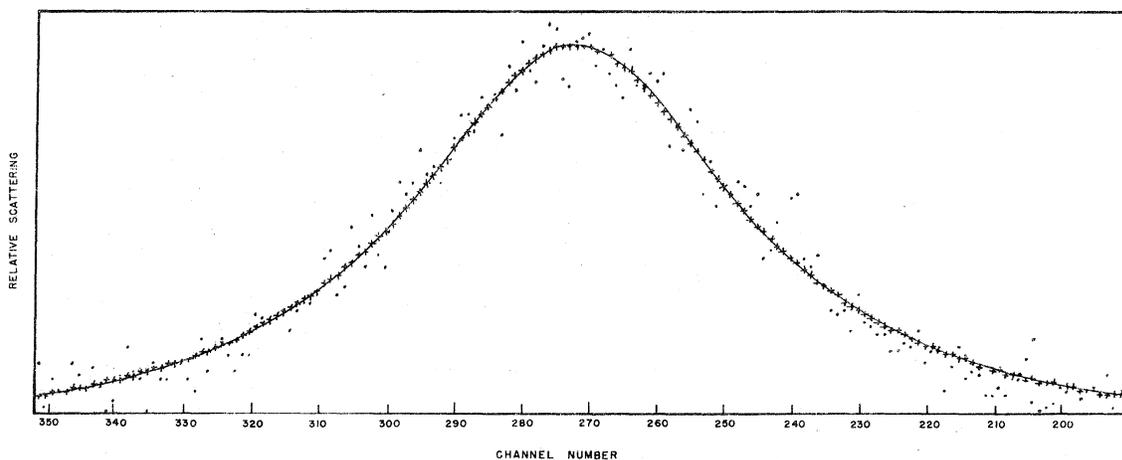

FIG. 1. FeAl backscattering run number 106a. The solid line is the least squares fit of a single Lorentzian to the data (solid points).

TABLE I. Results of charge-density calculations.

Compound	$\rho(0)$ (a_0^{-3}) 4s	Potential	Reference
TiFe	5.528	Papaconstantopoulos	9
Fe	5.178	Wakoh and Yamashita	7
Fe	4.911	Williams et al.	21
FeAl	4.480	Nagel et al.	10

The quantity of interest here is,

$$\rho_s(r) = \frac{1}{4\pi r^2} \sum_{nk} W_{nk} P_{nk}^2(r) , \qquad (4)$$

where W_{nk} is a weighting factor to account for the like vectors $\vec{k}$ in the Brillouin zone, $P_{nk}(r) = rR$ where R is the radial wave function of s character, and n is the band index. The summation in Eq. (4) is over occupied states only.

In order to calculate $\Delta\rho(0)$ we have utilized the charge densities at the nucleus, obtained by extrapolation of our APW results using a formula suggested by Wakoh and Yamashita, i.e.,

$$\rho_s(r) = A(12 - Zr) + Br^2 , \qquad (5)$$

where A and B are constants and $Z = 26$ the atomic number of Fe. The band-structure calculations for TiFe and FeAl have been done in the "frozen core" approximation, i.e., we have assumed that the $1s$, $2s$, and $3s$ charge densities remain unchanged between Fe and its compounds TiFe and FeAl. Thus, our results are based on the difference of the valence ($4s$-like) charge densities and are shown in Table I.

V. RESULTS AND DISCUSSION

Table II lists and Fig. 2 shows our measured values of isomer shift and calculated values of charge density with respect to Fe metal based on the Wakoh and Yamashita results. We expect that if a value for α would be extracted from this figure

TABLE II. Data shown in Fig. 2.

Compound	Charge-density differences (a_0^{-3})	Isomer shift[a] (mm sec^{-1})
TiFe	+0.617[b]	−0.145 ± 0.007[d]
TiFe	+0.350[c]	−0.145 ± 0.007[d]
FeAl	−0.698[c]	+0.272 ± 0.015
FeAl	0.431[b]	+0.272 ± 0.015

[a] With respect to Fe metal at 300 °K.
[b] With respect to Williams et al. (Ref. 21) Fe potential.
[c] With respect to Wakoh and Yamashita (Ref. 7) Fe potential.
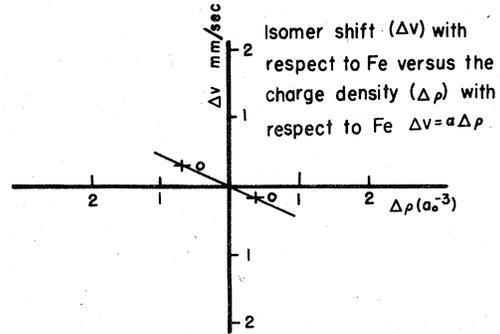[d] Reference 8.

FIG. 2. Isomer shift (Δv) with respect to Fe metal at 300 °K vs the charge density $\Delta\rho$ (0) with respect to Fe metal. + point—charge density with respect to Wakoh and Yamashita Fe potential. O points—charge density with respect to Williams et al. (Ref. 21) Fe potential.

it would be overestimated, since, as discussed in Sec. IV, we have neglected the charge-density differences of the core levels. Inclusion of the effect of the core levels would increase the total charge-density difference and therefore reduce α. In order to check the sensitivity of our calculations to the approximation made in the treatment of the exchange potential, we have performed an additional calculation for Fe metal, using the crystal potential of Williams et al.[21] This potential differs from that of Wakoh and Yamashita in that the exchange was treated according to the formalism of Hedin and Lundqvist,[22] and assumes Fe to be paramagnetic. The resulting charge density is also included for comparison on Fig. 2. The criterion for a crystal potential choice is decided by whether the straight line connecting the FeAl and TiFe points passes through the origin. It is seen that the charge-density calculation based on the WY potential fulfills the criterion better than the Williams et al. potential.[21] We regard this as an indication of the difficulty of performing a charge-density calculation at the nuclear site, rather than a criterion of the accuracy of the respective band calculations. The results of the TiFe calculation presented here differ slightly from that used in Ref. 8. In Ref. 8 we approximated $\rho_s(0)$ from the band wave functions at the point Γ (center of the Brillouin zone), while in the present work we obtained $\rho_s(0)$ by sampling 10 $\vec{k}$ points in the zone as discussed in Sec. IV.

VI. CONCLUSIONS

A value for α could be extracted from the graph of our work, Fig. 2. However, such a calculation would be based solely on three points and one type of charge-density calculation coordinated with one type of compound, metal alloys. This has been the
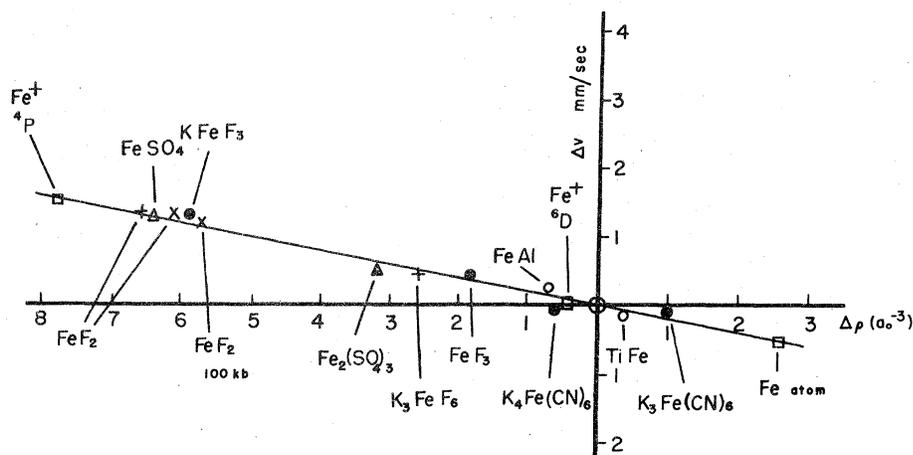
FIG. 3. Isomer shift (Δv) with respect to Fe metal at 300 °K vs the charge density with respect to Fe metal from several recent charge-density calculations. □ Points—Ref. 12; + points—Ref. 2; △ points—Ref. 4; ✘ points—Ref. 11 and 23; ● points—Ref. 13.

approach of the majority of authors and has been largely responsible for the wide range of α's appearing in the literature. In most cases only the Fe^{2+}, Fe^{3+} difference was calculated and used to get α. Instead, the present authors take the view that α should be calculated from a variety of both positive and negative isomer-shift materials, and calculational techniques. Thus, Fig. 3 gives a survey of several recent isomer-shift calibrations based on molecular-orbital calculations, the band-structure approach reported on here, and atomic-structure calculations. Besides our own work on TiFe and FeAl and the work of Duff on K_3FeF_6 and FeF_2, four recent isomer-shift calculations are included: (i) the calculation by Reschke et al.[11] coordinated with the isomer shifts reported by Champion et al., for FeF_2 pressure measurements[23]; (ii) the calculation by Bloomquist et al.[5] for the rare-gas matrix-isolation measurement by Micklitz and Litterst[12]; (iii) the $FeSO_4$ measurements reported by Havens and Noftle[24]; and (iv) The calculations and measurements by Nieuwpoort et al.[13] on the high- and low-spin ferrous and ferric compounds. Most of these data use different Fe atomic configurations. In order to present all these data on the same plot it was necessary to determine for each calculation the value of the charge density for zero isomer shift with respect to Fe metal. Thus, Fig. 3 summarizes the most recent work on charge densities and isomer shifts and includes data for both positive and negative isomer shifts, high-spin and low-spin ferrous and ferric compounds, and metal alloys. This figure also provides a visual understanding of how various calculations may individually give α's differing by a factor of 2. This kind of plot with the origin set at Fe metal is a simple

but useful plot. It forces the data from the two quadrants through the origins, i.e., the isomer shift of Fe with respect to Fe must be 0. Other work has presented a variety of origins making it difficult to assess the magnitude of the systematic differences between the calculations.

A realistic view of the current status of α, the calibration constant, and $\delta\langle r^2 \rangle$ is to give equal weight to all of these calculations, thus encompassing both band-structure, atomic-structure, and molecular-orbital calculations. A least-squares fit to a straight line for all this data plotted in Fig. 3 gives an α of -0.206 a_0^3 mm sec^{-1} and a $\delta\langle r^2 \rangle$ of 14.7×10^{-3} Fm^2. The standard deviation of the points from this line gives an error for the slope α of 8%. Researches investigating a series of ionic compounds, metal alloys or biological compounds could use this value of α to estimate within the limits of this error, the change in charge density for members of those compounds. It would however be unrealistic to presently assume that charge-density estimates based on only one type of calculation could yield a more accurate value.

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