$1/\tau$ is equal to λ_{0k}, the transition probability. Using the expression for the density-in-energy of final states given in (A.27),

$$\lambda_{0k}=\frac{N|M_{0k}|^2}{\pi\hbar^2\gamma}\left(\frac{4\pi M_0}{12H_e^3}\right)^{\frac{1}{2}}, \tag{A.28}$$

where M_{0k} is the matrix element of the scattering perturbation. If we represent the perturbation by a fluctuating effective magnetic field[1] $H(\mathbf{R})$, then

$$\lambda_{0k}=\frac{\gamma\langle S^2\rangle_{\text{av}}|H(\mathbf{k})|^2}{(12)^{\frac{1}{2}}\pi}\left(\frac{4\pi M_0}{H_e^3}\right)^{\frac{1}{2}}, \tag{A.29}$$

where $H(\mathbf{k})$ is the $\mathbf{k}$th Fourier component of $H(\mathbf{R})$.

Substituting (A.27) and (A.29) into expression (A.26) results in the requirement

$$\frac{1}{N-1}\frac{\langle(\Delta S)^2\rangle_{\text{av}}}{\langle S^2\rangle_{\text{av}}}\frac{N}{2\pi^2\gamma}\left(\frac{4\pi M_0}{12H_e^3}\right)^{\frac{1}{2}} \times\frac{\gamma\langle S^2\rangle_{\text{av}}|H(\mathbf{k})|^2}{\pi}\left(\frac{4\pi M_0}{12H_e^3}\right)^{\frac{1}{2}}\ll\frac{1}{2}, \tag{A.30}$$

or

$$\frac{N}{N-1}\frac{\langle(\Delta S)^2\rangle_{\text{av}}}{6\pi^2}\frac{M_0}{H_e^3}|H(\mathbf{k})|^2\ll\tfrac{1}{2}, \tag{A.31}$$

where it is to be recalled that $|H(\mathbf{k})|\approx10^6$. Inserting the values $4\pi M_0=5000$ gauss, $H_e=10^6$ oe, and setting $N/(N-1)=1$, we have

$$7\times10^{-6}\langle(\Delta S)^2\rangle_{\text{av}}\ll\tfrac{1}{2}, \tag{A.32}$$

which is certainly satisfied. Thus the corrections to the magnon scattering due to the nonorthogonality of the spin waves in a disordered ferrite are totally negligible.

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Absolute Measurement of the Atomic Scattering Factors of Iron, Copper, and Aluminum

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The x-ray atomic scattering factors of iron, copper, and aluminum were carefully remeasured to obtain more reliable information on the outer electron charge densities in these elements. The scattering factors were obtained from measurements of the integrated Bragg intensities of powder samples using monochromatic Mo K_α radiation. The intensities were put on an absolute scale by direct measurements of the power in the primary x-ray beam. Extinction, surface roughness, and preferred orientation effects were shown to be negligible in the samples used. The ratios of the measured scattering factors of the three elements agree with those calculated from Hartree-Fock theory to within 1%. This substantiates the findings of Batterman, and, in contrast with the previous results of Weiss and DeMarco, indicates that there is no large discrepancy between the electronic structures of copper and iron. The absolute values of the measured scattering factors, however, lie about 4% below theory in the region of low $\sin\theta/\lambda$. It is pointed out that the high theoretical values for iron and copper could result from known differences in electronic structure between a free atom and one in the solid, but that present theory probably cannot account for the discrepancy in the case of aluminum.

INTRODUCTION

In the past few years, several experiments have been undertaken to measure the electron distribution in the iron transition metals. The ultimate aim of these experiments is to help in the basic understanding of unresolved problem of the magnetism of these metals.

In these experiments the intensities of x-ray Bragg reflections are experimentally determined and reduced to charge densities by comparing the experimental form factors obtained from these intensities with those calculated from theoretical wave functions. Briefly, the chronology of these experiments is as follows: Weiss and DeMarco[1] made absolute measurements on single crystals of several transition metals and concluded that body-centered cubic iron and chromium have a deficiency of $3d$ electrons compared with the free atom. Batterman[2] measured relative intensities of powders of copper, iron, and rock salt and reported form factors in good agreement with calculations for the free atom and consequently disagreed with the Weiss and DeMarco results. Weiss and DeMarco[1] then repeated

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[1] R. J. Weiss and J. J. DeMarco, Revs. Modern Phys. **30**, 59 (1958); Phys. Rev. Letters **2**, 148 (1959).

[2] B. W. Batterman, Phys. Rev. Letters **2**, 47 (1959); Phys. Rev. **115**, 81 (1959).

Batterman's work and reconfirmed their original single-crystal measurements. Komura, Tomiie, and Nathans[3] reported absolute measurement of the iron form factor from an ordered single crystal of Fe_3Al. This did not confirm the Weiss and DeMarco results but gave approximate agreement with a free-atom calculation.

Each of these experiments involved different techniques and each technique has certain weaknesses which would add uncertainty to the reported experimental atomic scattering factors. The first Weiss and DeMarco results are subject to considerable uncertainty because of extinction effects. To correct for the fact that the single crystals used were not ideally imperfect, a theoretical extinction correction was applied, which, for the measurements on iron involved extrapolations of between 18 and 100% of experimental values. By using cold-worked powders, Batterman was able to eliminate extinction effects. However, the measurements were made with Fe K_α radiation for which the dispersion correction to the iron scattering factor is quite large. The accuracy of the reported scattering factor, F, is then subject to a considerable theoretical correction, the accuracy of which is difficult to estimate. Because of the difficulty in making absolute measurements on powders, Batterman's results for iron are relative to a theoretical form factor for copper or rock salt. It would be less ambiguous to make an absolute measurement of the atomic scattering factor f for a given element without having to rely upon the validity of a theoretical value for another material. Komura, Tomiie, and Nathans' work on an alloy of iron has the criticism that the electron density of iron in the alloy may not be the same as in pure iron. Their form factor values have the additional uncertainties inherent in a neutron diffraction determination of the long-range order parameter.

EXPERIMENTAL

The experiment reported in this paper was proposed to overcome the objections outlined above. It was decided that the only way to eliminate extinction effects was to use powders rather than single crystals. Here one can vary the perfection by cold-working and, by observing the intensities of the stronger reflections as a function of cold-working, it could be decided whether or not extinction was negligible. The measurements were made with Mo K_α x rays so that the dispersion (Hönl) corrections would be quite small. For example, the dispersion correction of Fe K_α radiation on the (110) iron form factor is the order of 2.4 units in 19 while for Mo K_α radiation it is only 0.3 in 19. Batterman[2] chose to use Fe K_α radiation despite the large Hönl correction because of the problem of surface roughness. The surface of the specimen if not perfectly flat will increase the effective absorption coefficient, the increase probably being larger at the lower Bragg angles. Fe K_α radiation puts the Bragg reflections at considerably higher Bragg angles than the Mo K_α. However, it was felt justified in the present experiment to use Mo K_α since there was available a method for independently checking whether or not the surface roughness effect was important. To eliminate the objections concerning the measurement of relative intensities the present results on iron, copper, and aluminum were placed on an absolute scale by directly measuring the primary beam intensity.

A Norelco diffractometer was modified to accept Mo K_α radiation monochromated with a cylindrically bent LiF crystal. The focal point of the bent crystal was at the normal entrance slit to the spectrometer. The detector consisted of a NaI thallium-doped scintillation counter used in conjunction with a pulse-height analyzer. A separate detector monitored the beam intensity at all times. Multiple-foil techniques were used to check carefully on the linearity of the detector and established that the over-all dead time was 4.4 μsec, which corresponded to an error of less than 1% at 2000 cps. The dead-time correction was applied to all counting rates in excess of 1000 cps. Enough intensity for good statistics was obtained by operating at 31 kv and 20 ma which did not excite the half-wavelength harmonic. Intensity measurements were made using symmetrical reflections from the face of a compressed powder thick enough to absorb the entire beam. The θ-2θ relationship between sample face and counter slit was adjusted to be symmetrical to 0.2° in 2θ. Serious intensity errors can result for low-angle reflections if this adjustment is not accurate.

The iron specimens were made from carbonyl iron containing particles the order of 3–5 micron diameter and purity 99.5%. The copper specimens were of electrolytic powder of 99.2% purity and about 5 μ particle size. The aluminum powder had a particle size of approximately 5–10 microns and purity of 99.6%.

The powders were pressed in a highly polished mold into disks the order of 0.3 cm thick and diameter of 1.5 cm which could fit conveniently into the sample spinner attachment to the diffractometer.

Preferred orientation was checked by observing the variation of integrated intensity of several reflections with molding pressure. The pressure ranged from one just sufficient to hold the powder together (the order of one psi) to a maximum of 120 000 psi for iron, 60 000 psi for copper and 30 000 psi for the aluminum. The generally observed behavior of iron and copper was a change in intensity of about 5%, either increase or decrease depending on the reflection, from the highest pressures down to several thousand psi. The variation from zero up to 30 000 psi was the order of 2%. At pressures less than a few thousand psi, the intensities of all reflections decreased, regardless of the sign of the variation of intensity with pressure, this decrease was due to surface roughness absorption. For

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[3] Y. Komura, Y. Tomiie, and R. Nathans, Phys. Rev. Letters **3**, 268 (1959); J. Phys. Soc. Japan **15**, 1434 (1960).

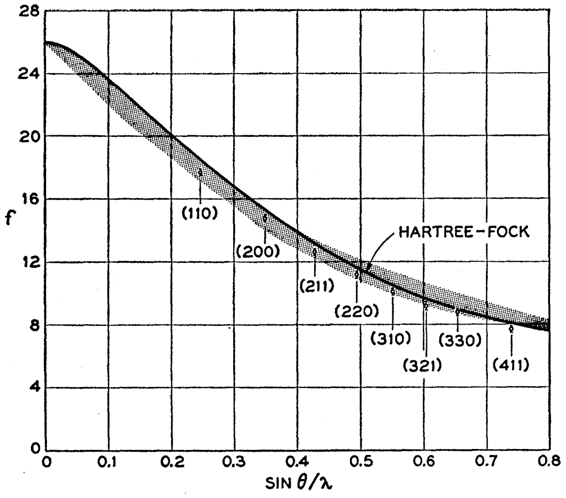

FIG. 1. Absolute experimental scattering factor for iron. The H-F curve is taken from reference 7, and the shaded region encompasses the Hartree and T-F-D factors of references 8 and 9.

copper and iron the surface roughness was independently measured by comparing the fluorescence scattering from the powder at a low Bragg angle (far from any Bragg reflection) with that from a highly polished slug of the same material. Where surface roughness was present, the fluorescence from the powder was less than from the polished specimen.

By comparing the surface roughness fluorescence and the integrated intensity as a function of pressure (and consequent cold working) samples could be picked which were free of preferred orientation, extinction and surface roughness. A further check on extinction was to cold work powders before compression to put in added cold working. This succeeded in further broadening the reflections but did not significantly affect the integrated intensities. Preferred orientation and surface roughness in aluminum were shown to be negligible by comparing reflections from the face of a powder disk to the same reflections measured in transmission.

The integrated intensities on a relative basis were taken in the following way: Using a standard receiving slit at the counter, the total number of counts was recorded as the spectrometer was driven with uniform angular velocity through a range that included the tails of the reflections. Counts were taken on each side of the reflection and the average used to correct for background.

TABLE I. Experimental and calculated parameters used to evaluate atomic scattering factors.

	$a_0(A)$	$(\mu_\rho cm^2/g)$	$\Delta f'$	B[a]
Iron	2.8664	37.46	+0.35	0.3589
Copper	3.6147	49.24	+0.35	0.5429
Aluminum	4.0496	5.019	+0.1	0.8528

[a] Based on Debye θ of 425°K, 320°K, and 395°K for Fe, Cu, and Al, respectively.

To put the relative intensities on an absolute basis the total power in the primary beam was measured, using three independent methods. The experimental details of the absolute measurements will be given in the Appendix. All three methods gave primary beam powers that agreed to within 2%.

The absolute integrated intensity of the iron (110) reflection was measured using a circular slit of silver of known area. Combining this result with the measured primary beam intensity, all data taken relative to the iron (110) could be put on an absolute basis.

It can be shown[4] that the integrated intensity from a powder can be expressed as

$$\frac{E\omega}{I}=\frac{nN^2}{\mu}\left(\frac{e^2}{mc^2}\right)^2\frac{A\lambda^3}{32\pi R^2}F^2\frac{(1+\cos^2 2\theta_M\cos^2 2\theta)}{\sin^2\theta\cos\theta(1+\cos^2 2\theta_M)},\qquad(1)$$

where ω is the angular velocity, and A the area of the slit; e^2/mc^2 the classical electron radius; F, the room temperature structure factor; R, the receiving slit to specimen distance; λ, the x-ray wavelength; n, the multiplicity; θ_M, the monochromator angle; N, number of unit cells per unit volume; μ, linear absorption coefficient; E, total energy diffracted into the counter and I the power in the primary beam. Using experimental values for E, ω, I, A, R, and μ, the structure factor, F, can be experimentally determined on an absolute basis. For our materials, F is related to the atomic scattering factor, f_0, by

$$F=n_0|f_0+\Delta f'+i\Delta f''|\exp(-M)(1+\alpha),\qquad(2)$$

where n_0 is the number of atoms in the unit cell, the

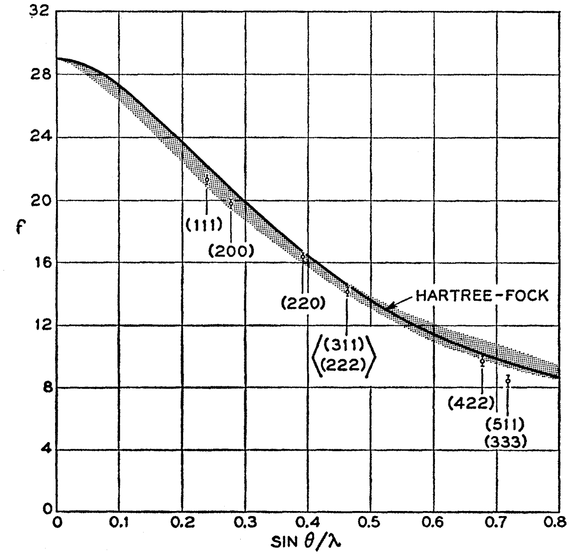

FIG. 2. Absolute experimental scattering factor for copper. The H-F curve is taken from reference 7, and the shaded region encompasses the Hartree and T-F-D factors of references 8 and 9.

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[4] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1950).

TABLE II. Absolute experimental atomic scattering factors for iron, copper, and aluminum.

Iron			Copper			Aluminum		
hkl	f_{exp}	$f_{\text{theory}}{}^{\text{a}}$	*hkl*	f_{exp}	$f_{\text{theory}}{}^{\text{a}}$	*hkl*	f_{exp}	$f_{\text{theory}}{}^{\text{a}}$
110	17.63±0.20	18.50	111	21.29±0.34	22.20	111	8.63±0.14	9.03
200	14.70±0.23	15.33	200	19.75±0.34	20.78	200	8.25±0.14	8.60
211	12.62±0.21	13.20	220	16.37±0.30	16.77	220	7.09±0.13	7.37
220	11.13±0.20	11.63	(311/222)[b]	14.14±0.27	14.69	311	6.42±0.12	6.69
310	10.10±0.19	10.55	422	9.69±0.38	10.17	222	6.19±0.13	6.50
222	9.13±0.25	9.66	511–333	8.37±0.40	9.58	400	5.48±0.15	5.79
321	8.75±0.19	9.05				331	4.96±0.14	5.34
411–330	7.68±0.21	8.12				420	4.67±0.13	5.20
						422	4.38±0.15	4.69
						511–333	4.00±0.16	4.38

[a] See reference 7.
[b] The (311) and (222) reflections of copper were measured as a single peak. The scattering factor is given at the weighted value of $\sin\theta/\lambda$.

$\Delta f'$ and $\Delta f''$ are the real and imaginary Hönl corrections, $\exp(-M)$ the Debye factor, $M = B(\sin^2\theta)/\lambda^2$, and α is a small correction[5] for the thermal diffuse scattering that peaks directly beneath the Bragg reflection. $\Delta f'$ was calculated according to the method of Parratt and Hempstead[6] ($\Delta f''$ is negligible). In Table I are given the parameters used in Eqs. (1) and (2) to evaluate the form factors from the experimental intensities. Figures 1, 2, and 3 and Table II give the present experimental values for the total absolute atomic scattering factors of iron, copper, and aluminum, together with the results of Hartree-Fock[7] calculations for the free neutral atoms. The shaded areas in the figures represent the regions included by the Hartree[8] calculations (without exchange) and the statistical Thomas-Fermi-Dirac[9] treatment.

DISCUSSION OF RESULTS

It was first pointed out by Weiss and DeMarco that a measurement of the x-ray form factor might provide information on the outer (3*d*) electron distribution in the iron transition metals. These electrons are responsible for the magnetic properties of these metals. It follows then, that the lower order reflections are the most significant because they are the most sensitive to the outer electron distributions. Fortunately, these reflections have the smallest statistical uncertainties because of their high intensities and favorable signal-to-noise ratios. For the lowest order reflection of each of the three materials investigated, the combined uncertainty on the absolute values is estimated to be ±1.5%, while the relative form factors have an uncertainty of ±0.5%. The higher order form factors have uncertainties from two additional sources. The intensities of these reflections are weak and the signal-to-noise ratios are lower so that the statistical uncertainties in the experimental intensities are high. In addition, the absolute form factors depend more strongly on the Debye-Waller factor $\exp(-M)$ and the correction α [see Eq. (2)] for the thermal diffuse scattering under the Bragg reflections. This latter correction ranges from 0.3% to 3% for iron, 0.4 to 4.3% for copper, and 0.5% to 4.8% for aluminum, the percentages increasing monotonically with $\sin\theta/\lambda$. The

TABLE III. Relative atomic scattering factors of iron, copper, and aluminum.

Iron			Copper			Aluminum		
hkl	$f_{\text{exp}}{}^{*}$	$f_{\text{theory}}{}^{\text{a}}$	*hkl*	$f_{\text{exp}}{}^{*}$	$f_{\text{theory}}{}^{\text{a}}$	*hkl*	$f_{\text{exp}}{}^{*}$	$f_{\text{theory}}{}^{\text{a}}$
110	18.38	18.50	111	22.19	22.20	111	9.00	9.03
200	15.32	15.33	200	20.59	20.78	200	8.60	8.60
211	13.16	13.20	220	17.06	16.77	220	7.39	7.37
220	11.60	11.63	311	14.74	14.69	311	6.69	6.69

[a] See reference 7.

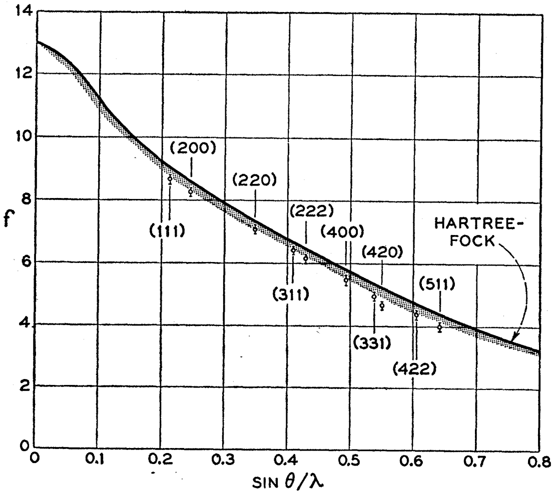

FIG. 3. Absolute experimental scattering factors for aluminum. The region between the H-F curve (reference 7) and the Hartree calculation (reference 8) is shaded.

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[5] D. R. Chipman and A. Paskin, J. Appl. Phys. **30**, 1998 (1959).
[6] L. G. Parratt and C. F. Hempstead, Phys. Rev. **94**, 214 (1954).
[7] The Hartree-Fock values for aluminum are from A. J. Freeman, Acta. Cryst. **12**, 261 (1959); for copper from J. Berghius *et al.*, Acta Cryst. **8**, 478 (1955) and are for Cu^{+}. The neutral-atom value was obtained by adding the 4*s* form factor used by A. J. Freeman, Acta. Cryst. **12**, 274 (1959). The iron values are values from A. J. Freeman and R. E. Watson, Acta. Cryst. (to be published.
[8] H. Vierroll and O. Ögrim, Acta. Cryst. **2**, 277 (1949).
[9] L. Thomas and K. Umeda, J. Chem. Phys. **26**, 293 (1957).

uncertainties in all the experimental form factors are indicated by the error bars in the figures and in Table II.

Before discussing the discrepancy between the experimental values and theory, however, we note that the three experimental curves can be viewed as a set of relative measurements, without considering the absolute standardization. In the following sections we will compare the data with the latest Hartree-Fock (H-F) theoretical scattering factors as the most widely accepted theoretical calculations to date. Table III results from increasing the data of Table II by a constant factor 1.042, determined to give the best over-all fit to the H-F theory. The table compares these measured relative values with the theoretical f factors, for the first four reflections of each element. The agreement is quite good, being well within experimental error for all reflections shown, although it becomes poorer for higher order reflections, probably because of the uncertainty in the Debye-Waller factor and the correction for thermal diffuse scattering.

Some important conclusions can be drawn directly from the data of Table III. Weiss and DeMarco found agreement between the measured and theoretical scattering factors for copper, but measured a value for iron which was about 12% below theory at the first reflection. They interpreted this as indicating that iron has 2.3 ($3d$) electrons in the solid as compared with six for the free atom. Batterman subsequently reported that he found the ratio of the scattering factors of iron and copper very close to that predicted by H-F calculations for the free atom. Our present measurements, using a shorter x-ray wavelength which reduced the dispersion correction, confirm the results of Batterman. Hence we conclude that the large differences in the electron distribution in the metallic states of iron and copper reported by Weiss and DeMarco do not exist.

Although the relative measurements agree well with free-atom theory, we cannot conclude from this that the electron distributions of the individual metals, iron, copper, and aluminum, are essentially like those of the free atoms. To answer this question we must resort to the absolute measurements of the scattering factors as shown in Figs. 1, 2, and 3. The experimental points shown in these figures do not agree with H-F theory within the estimated probable error. For the form factors at lower values of $\sin\theta/\lambda$, which are of particular importance in determining the outer electron distribution, the discrepancy between theory and experiment is about 4.2% in f, (or 8.5% in the measured intensities which are proportional to f^2), for each of the atoms, iron, copper, and aluminum. The estimated statistical error is approximately $\pm 1.5\%$ in f.

Thus we are faced with a real discrepancy between theory and experiment. This discrepancy can be associated with one or more of the following considerations: (1) There is an error beyond the estimated statistical errors in one or more of the measured quantities in Eq. (1); (2) the present experiment has not satisfied all the conditions for which the mosaic crystal formula [Eq. (1)] has been derived; (3) the experimental form factors are accurate and the discrepancy lies within the theoretical scattering factors. A fourth possibility exists, namely that the mosaic crystal formula is incorrect even for the ideal conditions for which it was derived. The question of the validity of the mosaic crystal formula will not be examined here. The formula is widely accepted, but no experimental proof of its accuracy to the degree necessary in the present work exists. However, lacking any direct evidence of error in the formula, it will be accepted as being correct.

The fact that a uniform 4.2% adjustment puts all of the data into agreement with theory (Table III) suggests that a single error is responsible for these differences [condition (1) above]. Consequently, a considerable effort has been devoted to cross-checking the various parameters appearing in the equation. With the exception of the primary beam intensity, I_0, the parameters are all quantities which involve quite straightforward measurements, and the total probable error from these cannot be sufficient to account for the difference. The exact measurement of I_0 is very difficult. However, after finding agreement among several independent methods for measuring I_0, we conclude that the total experimental error remains insufficient to explain the observed difference between theory and experiment.

Granting the above, it is still possible that the formula may not apply in the cases where we have used it [condition (2)]. The formula assumes no extinction, no preferred orientation, no surface roughness absorption, and assumes ideal geometry such as symmetrical reflection and proper focusing. However, we believe that the checks discussed in the preceding section have shown the effects of these considerations to be negligible in the experiments as performed.

There are few recent data in the published literature with which we can compare our results. However, recent absolute measurements of atomic scattering factors of two of the elements which we have used are available for comparison. These are the data of Bensch, Witte, and Wölfel[10] on aluminum, and the results of Komura, Tomiie, and Nathans[3] on Fe_3Al. The data of Bensch *et al.* must be adjusted by the subtraction of

TABLE IV. Experimental and theoretical atomic scattering factors for aluminum.

f \ hkl	111	200	220	311	222
$f_{(\mathrm{exp})}$	8.63	8.25	7.09	6.42	6.19
f_{exp}(Bensch *et al.*)	8.55	8.24	7.15	6.48	6.38
f_{theory}(H-F)	9.03	8.60	7.37	6.69	6.50

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[10] H. Bensch, H. Witte, and E. Wölfel, Z. Physik Chem. 4, 65 (1955).

TABLE V. Experimental and theoretical atomic scattering factors for iron.

$\sin\theta/\lambda$ \ f	0.150	0.173	0.286	0.299	0.449
f_{exp}	20.97	20.19	16.53	16.12	12.16
f_{exp}(Komura *et al.*)	20.87	20.32	16.62	16.29	12.27
f_{theory}(H-F)	21.85	21.04	17.23	16.81	12.68

0.1 electron Hönl dispersion correction to be comparable with ours. Komura *et al.* have measured reflections of Fe_3Al involving the difference of the iron and aluminum scattering factors, and used the H-F values for aluminum to obtain their final values for iron. We have adjusted their data using our values for f_{Al} to obtain a true experimental value for f_{Fe}. These comparisons are made in Tables IV and V. The results for both iron and aluminum lie much closer to the present experimental values than to the H-F theory, lending support to the contention that a real discrepancy exists.

This leaves us with condition (3) where the H-F calculations are to be considered. If it is assumed that the H-F calculation for the free atom is sufficiently accurate, one can attempt to explain the discrepancy as a result of an altered electronic structure for the atom in the solid. Wood[11] and Stern[12] have calculated the outer electron wave functions of iron in the solid. Their results indicate a spreading out of the $3d$-electron distribution which would reduce the form factors of the lower order reflections in qualitative agreement with the present results for iron and copper. However, one would not expect this effect to be as large for aluminum.

The observed scattering factors for aluminum are actually lower than the H-F scattering factors for the neon core alone, thus implying that a substantial redistribution of the core electrons is required in this case. Although such a redistribution is not impossible, it would perhaps be equally fruitful to question the accuracy of the H-F calculation for the free atom.

Finally, we would like to reiterate that the data cannot be used to extract the number of $3d$ electrons in metallic iron as was attempted by Weiss and DeMarco. Using the recent calculations of Watson and Freeman[13] for the scattering factors of free iron with different numbers of $3d$ electrons, the present data would give approximately four $3d$ electrons per atom. The calculations of Wood[11] and Stern[12] indicate that when the effects of the band structure of the solid are included, a considerable spreading of the $3d$-electron wave functions occur, particularly for states near the bottom of the $3d$ band. Stern has shown, for example, that solid iron with seven $3d$ electrons per atom has a lower scattering factor that free iron having six such electrons, at the angle of the first Bragg reflection. Hence, without more exact information of this sort, one will not be able to locate $3d$ electrons from scattering factor data.

In summary we have found that: (1) The results of Weiss and DeMarco showing a large difference in electronic structure between iron and copper could not be reproduced and must be assumed to be in error. This is in agreement with the conclusions of Batterman, and of Komura, Tomiie, and Nathans. (2) The absolute values of the scattering factors of iron, copper, and aluminum were each found to be lower than predicted by Hartree-Fock theory, by about 4% in the region of the first Bragg reflections, but no ready explanation for this difference is available, particularly in the case of aluminum.

ACKNOWLEDGMENTS

The authors are indebted to R. J. Weiss for continued encouragement and advice and for concurrent but independent corroboration of some of the absolute scattering factor measurements. They also thank L. D. Jennings and A. Paskin for many valuable suggestions and criticism. They thank A. J. Freeman for the use of unpublished scattering factors.

APPENDIX I

This section describes the techniques used to measure the total power in the primary x-ray beam. The beam as used in these experiments contained about 2×10^7 counts per second of nearly monochromatic Mo K_α radiation with a total angular divergence of about one degree. At the distance of the x-ray counter, the beam had a cross section of about 5×10 mm. The scintillating crystal in the counter had an area of uniform receiving sensitivity greater than 15×15 mm, so that the entire beam could be counted at one setting of the receiver, except that the counting rate would then be much too high. Multiple-foil linearity checks established the over-all dead time of the counting circuitry as 4.4 microseconds, which makes the dead time correction at a counting rate of 4000 counts per second less than 2%. This counting rate was the maximum which was allowed to occur throughout the course of the experiment. The main problem in the absolute standardization of the data, then, is the reduction of the primary beam by an accurately known factor of about 10^4. This has been done by three essentially independent methods.

The first method involved an attenuation of the beam using a set of zirconium absorbers, each of which reduced the beam by a factor of about nine. The attenuation coefficient of each foil was measured separately, and five foils were used in series to reduce the beam to a countable level. Extreme care is needed when so high an attenuation is required because the primary beam is never completely monochromatic. Wavelength impurities, in addition to the half-wavelength component

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[11] J. H. Wood, Phys. Rev. **117**, 714 (1960).

[12] F. Stern, Phys. Rev. **116**, 1399 (1959); Bull. Am. Phys. Soc. **5**, 456 (1960).

[13] R. Watson and A. J. Freeman, Acta. Cryst. **14**, 27 (1961).

(avoided here by operating the x-ray tube at 31 kv), can arise from fluorescence and other scattering from the slits and monochromating crystal holder, from Compton and thermal scattering from the monochromating crystal, and from a small band of wavelengths near the K_α line diffracted from the continuous spectrum and not removed by the slit system. A first attempt to measure the primary beam using aluminum absorbers failed because the very small component of shorter wavelengths present was greatly amplified relative to the K_α component by the λ^3 dependence of the absorption coefficient of aluminum. For zirconium absorbers, however, with the x-ray tube operated at 31 kv, the attenuation of all wavelengths shorter than the zirconium edge is greater than for the K_α radiation. (A check can be made for this type of hardening of the x-ray beam by comparing the attenuation of a foil measured in the nearly pure K_α radiation and then in series with the five absorbers.)

A second method for measurement of the primary beam, suggested by Weiss, utilized a pinhole in a silver slit as an attenuator. The power through the pinhole could then be measured using only one zirconium absorber. The diffuse scattering, principally fluorescence, from a single crystal of germanium was measured at a given spectrometer angle with the pinhole in the primary beam. Removing the pinhole, and using only one zirconium absorber, the diffuse scattering could again be measured. From the ratio of the diffuse scattering, and the attenuation coefficient of the zirconium absorber, the primary beam power can be calculated. With this technique only one zirconium foil is needed at one time, rather than the five required in the first method. Hence, if alteration of the wavelength distribution is occurring, the effect should be quite different in the two cases.

A third method, in which the primary beam is measured without the need for absorbers, was developed to overcome the difficulty just mentioned. Here use is made of the very narrow width of the Bragg reflection of a perfect crystal. The power in the primary beam is spread over a divergence of about one degree. A perfect crystal of silicon has a natural reflecting width for Mo K_α of about three seconds of arc. A single crystal of silicon, set so that its Bragg angle lies within the one degree primary divergence, will diffract a beam whose intensity is low enough to be measured without the need of an absorbing foil. The integrated intensity of a particular silicon reflection is then measured by rotating the crystal with uniform angular velocity through the reflecting region and collecting all the diffracted intensity with a wide open scintillation detector. A separate measurement of the diffracting power of the crystal is then made in the following way: With very narrow slits, the primary beam is reduced to a countable rate, and then the total diffracted power is measured as above. Note that because of the small reflecting range of the crystal, the diffracted intensity is still comparable to the value before introducing the narrow slits. Using this experimentally measured reflecting power, and the integrated Bragg reflection without the narrow slits, the primary beam without the slits can be calculated. It should be noted that this method does not require knowledge of any theoretical form factor.

The three methods of standardization gave primary beam powers which agreed with one another to within 2%. Thus any of the methods, alone, would be satisfactory, but we tend to favor the perfect crystal method as the easiest and surest of the three. It might be noted that once the reflecting power of the silicon crystal has been measured as described above, this crystal can be used to standardize Bragg integrated intensity data obtained with nonmonochromatic x rays from a standard diffractometer, since the crystal "sees" only the K_α component in the beam.