Unpaired Spin Density in Ordered Fe₃Al†

S. J. Pickart

U. S. Naval Ordnance Laboratory, Silver Spring, Maryland and Brookhaven National Laboratory, Upton, New York

AND

R. Nathans

Brookhaven National Laboratory, Upton, New York

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A precise determination of the magnetic form factor of the ordered alloy Fe₃Al has been made by diffraction of polarized neutrons from a single crystal. Some 43 reflections in the angular range $\sin\theta/\lambda \leq 0.9$ A⁻¹ have been examined and show characteristic departures from a smooth single-valued function, indicating that the unpaired electron density in the unit cell is not spherically symmetric. The data are analyzed in two ways: by comparison with form factors calculated from free-atom Hartree-Fock wave functions including crystal-field splitting effects, and by two-dimensional Fourier projections of the unpaired spin density. The analysis indicates that, while the two types of iron atom in the lattice have similar radial spin densities, their orbital symmetry is different. The results are discussed with reference to various theories of the electronic structure in transition metals.

I. INTRODUCTION

NEUTRON diffraction methods furnish information about the electronic structure of ferromagnetic metals and alloys by determining both the magnitude of the atomic moment and the variation of the magnetic scattering cross section with angle. This latter quantity, the magnetic form factor, is the Fourier transform of the scattering density and so may be used to obtain the spatial distribution of the unpaired $3d$ electrons. Such an experimentally derived density function may then be compared with that predicted by theoretical models employing wave functions of various symmetry.

The neutron diffraction measurements of iron-group metals and alloys reported by Shull and co-workers[1] were concerned primarily with evaluation of the magnetic moments, although general features of the form factor were presented. These measurements were in the main carried out on polycrystalline material with unpolarized neutron beams. More recently, the polarized beam method was used by Nathans *et al.*[2] to determine the form factors of Fe, Ni, and Co single crystals. An interesting feature of these latter results was an indication that some of the higher angle reflections departed from a smooth f curve appropriate to a spherically symmetric spin density.

These irregularities have been attributed by Weiss and Freeman[3] to crystal field effects, which lift the degeneracy of the d orbitals and split them into two sets, a doublet having e_g symmetry and a triplet having t_{2g} symmetry. Such splitting has been appealed to in various theories, for example those given by Mott and Stevens[4] and Goodenough,[5] as a basis for dividing the d band in metals into bonding (conducting) subbands with diffuse wave functions and nonbonding subbands whose wave functions have a more localized character. On the other hand, the band structure calculations of Leigh,[6] Callaway and Edwards,[7] and Wood[8] indicate that cubic field splitting in metals is small compared to the d bandwidth.

With reference to these questions, it would, of course, be helpful to obtain meaningful projections of the electron density in metals by Fourier inversion of diffraction data. These would illustrate directly any departure from spherical symmetry and/or movement of electrons into bonds. Practical limitations on the amount and precision of available data have militated, in the past, against such a procedure. With neutron magnetic scattering, however, the interaction is only with electrons having unpaired spins, and this restriction, in addition to the much increased sensitivity of the polarized beam technique, offers more hope of success.

The present work describes an effort to measure a magnetic form factor in some detail, with a view toward Fourier inversion of the data. The choice of the ordered alloy Fe₃Al was made primarily because of its superstructure, which as a consequence of the greater density of points in reciprocal space provides a more thorough sampling of the charge in various symmetry directions. This advantage is of course offset by the presence of the aluminum, since more atoms must be resolved, but at the same time it allows an investigation of the way the alloy atoms affect the Fe moment and spin density.

We first discuss in Sec. II the crystal structure of the ordered state of Fe₃Al and review the previous

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[1] C. G. Shull, E. O. Wollan, and W. C. Koehler, Phys. Rev. **84**, 912 (1951); C. G. Shull and M. K. Wilkinson, Revs. Modern Phys. **25**, 100 (1953) and Phys. Rev. **97**, 304 (1955).

[2] R. Nathans, C. G. Shull, G. Shirane, and A. Andresen, J. Phys. Chem. Solids **10**, 138 (1959); R. Nathans and A. Paoletti, Phys. Rev. Letters **2**, 254 (1959).

[3] R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959).

[4] N. F. Mott and K. W. H. Stevens, Phil. Mag. **2**, 1364 (1957).

[5] J. B. Goodenough, Phys. Rev. **120**, 67 (1960).

[6] R. S. Leigh, Proc. Phys. Soc. (London) **71**, 33 (1958).

[7] J. Callaway and D. M. Edwards, Phys. Rev. **118**, 923 (1960).

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

polarized neutron work on this material. In Sec. III the experimental procedure is described and the data presented, along with a discussion of the factors affecting their accuracy, such as Debye temperature corrections, extinction, depolarization, and multiple-scattering effects. Analysis of the data, given in Sec. IV, proceeds along two paths: comparison of the observed form factors with those calculated from free-atom Hartree-Fock wave functions, including crystal field effects; and construction, by Fourier difference methods, of projections corresponding to the principal zone in which data were collected. Various factors contributing to the reliability of these density maps are considered, mainly series termination or diffraction effects. We conclude that asphericities in the spin density may be unambiguously demonstrated, and discuss what bearing the results may have on various theories of d electron states in metals.

II. Fe₃Al STRUCTURE

In the course of an investigation of the Fe−Al alloy system, Bradley and Jay,[9] using x-ray methods, discovered the formation of an ordered superstructure near the composition Fe₃Al. The ordering can be described as the systematic replacement of half the body-centered atoms in α-Fe by Al, in such a way that the corner Fe sees four Fe and four Al near-neighbor atoms, each in a tetrahedral coordination. In the stoichiometric, perfectly ordered alloy, the unit cell is as represented in Fig. 1. The supercell is composed of four interpenetrating fcc lattices, two occupied by Fe(II) atoms with
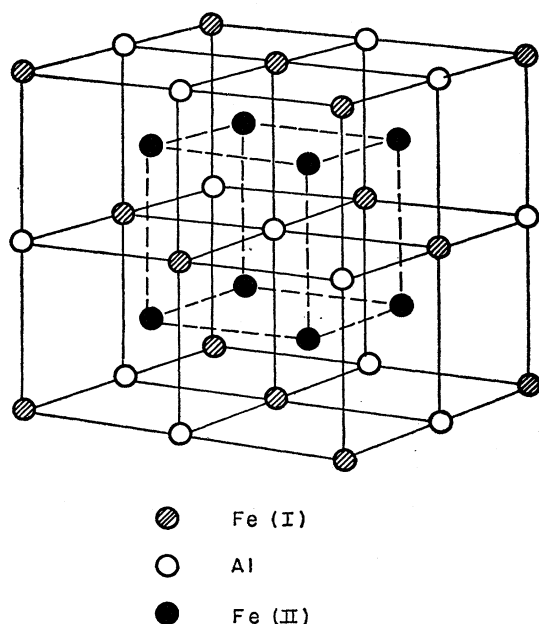

⊘   Fe (I)

○   Al

●   Fe (II)

FIG. 1. The ordered Fe₃Al lattice.

[9] A. J. Bradley and A. H. Jay, Proc. Roy. Soc. (London) A136, 210 (1932).

their origins at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$, and the other two by Fe(I) and Al with origins at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, respectively. The structure factors are related to the atom positions as follows:

h,k,l odd, $F=4(a_{\text{Fe(I)}}-a_{\text{Al}})$;

h,k,l even, $(h+k+l)/2$ odd,

$$F=4(a_{\text{Fe(I)}}+a_{\text{Al}}-2a_{\text{Fe(II)}});$$

h,k,l even, $(h+k+l)/2$ even,

$$F=4(a_{\text{Fe(I)}}+a_{\text{Al}}+2a_{\text{Fe(II)}});$$

where a is the scattering amplitude, nuclear or magnetic. These expressions assume that the two Fe(II) atoms are identical. This assumption or an equivalent one is necessary to determine the structure completely, and the consequences of adopting it are discussed later.

It is seen that the first two reflection types are superstructure lines, related to the difference in scattering between the body-center sites of the original cell and between the corner and body-center sites. The third type comprises the fundamental reflections which are related to the average scattering per atom in the unit cell. The superlattice structure factors are slightly different if there is some small degree of disorder, but the order parameters enter the magnetic and nuclear structure amplitudes in the same way. They are needed only to relate the scattering amplitude per crystallographic site to that per atom.

This composition was studied by Nathans et al.,[10] using neutron diffraction, in order to determine the effect of the environment on the moment of the Fe atoms and correlate any changes with magnetization measurements. Powder measurements indicated a difference between the moment of the Fe atom with only Fe near neighbors [Fe(I)] and that of the Fe atom with both Fe and Al near neighbors [Fe(II)]. This difference was put on a more quantitative basis by a single crystal study using an incident polarized beam,[11] the results being

$$\mu_{\text{Fe(I)}}=(2.18\pm0.10)\mu_B, \text{ and } \mu_{\text{Fe(II)}}=(1.50\pm0.10)\mu_B.$$

The Al moment was found to be zero.

In determining these moment values, only reflections of order lower than (400) were measured $(\sin\theta/\lambda\leq0.35$ A⁻¹$)$, and the magnetic form factor for metallic iron was adopted. As a justification of this procedure it was pointed out that ratios of the magnetic scattering amplitudes of successive reflections having the same structure factor were quite close to equivalent ratios taken from the iron form-factor curve. In other words, in this angular region no sizeable difference was apparent between the shapes of the Fe₃Al and the Fe

[10] R. Nathans, M. T. Pigott, and C. G. Shull, *Proceedings of the Conference on Magnetism and Magnetic Materials, Boston, 1956* (American Institute of Electrical Engineers, New York, 1957), p. 242.

[11] R. Nathans, M. T. Pigott, and C. G. Shull, J. Phys. Chem. Solids 6, 38 (1958).

metal form factor. This similarity was also borne out in a measurement of the x-ray scattering factor by Komura et al.[12]

Such a situation is not unexpected in view of the calculations of Weiss and Freeman,[3] who show that the effect on form-factor curves of asphericities in the d-electron charge distribution is insignificant for $\sin\theta/\lambda < 0.3$ A^{-1} and maximum in the region $\sin\theta/\lambda \sim 0.8$ A^{-1}. Consequently, any asphericity in the magnetic electron density or any difference between the density of the two iron types will not be noticed in measurements confined to low angles as in these previous studies.

III. EXPERIMENTAL METHOD AND RESULTS

1. Polarized-Beam Method

Since the polarized neutron diffractometer has been described elsewhere,[2] we give only the brief background necessary for discussion of the present results. For a given Bragg reflection, we obtain, by reversing the incident neutron polarization, the ratio

$$d\sigma_+/d\sigma_- = (1+\gamma)^2/(1-\gamma)^2,$$

where $\gamma = p/b$, the ratio of the magnetic to the nuclear structure factor. The sensitivity of this method results from the fact that the coherence between magnetic and nuclear scattering amplitudes is retained, while the absence of the necessity for determining a scale factor and measuring the integrated intensity makes the procedure relatively simple.[13] A knowledge of the chemical structure is, of course, necessary in order to calculate the nuclear structure amplitude, a straightforward procedure in the case of Fe₃Al if the state of order is known. Since the present specimen was cut from the same crystal as that used in the previous study,[11] we use, as was done there, the ordering scheme given by Bradley and Jay.[9] The observed ratio must be adjusted to allow for incomplete polarization of the incident beam (~ 0.95), for incomplete polarization reversal (~ 0.98), and for depolarization within the scattering crystal (normally small for single crystals). These corrections have been carried out according to the manner developed previously.[2]

2. Experimental Results

The measurements were made on two crystals cut from a common disk with a (100) face. They were in the shape of square pillars, roughly 2×2 mm in cross section and 1–2 cm in length, one cut with its long axis approximately [110] and the other [100]. The original crystal was grown from the melt and given a heat treatment necessary to achieve the ordered condition. A total of 43 reflections was examined, which includes all

[12] Y. Komura, Y. Tomiie, and R. Nathans, Phys. Rev. Letters 3, 268 (1959).

[13] R. Nathans, J. Appl. Phys. 31, 350S (1960).

those accessible in the two mentioned zones under $\sin\theta/\lambda \leq 0.9$ A^{-1}, the experimental limit of the spectrometer. Studies were carried out at three wavelengths (0.80, 1.05, and 1.27 A) at room temperature, though a few measurements were also made at 77°K.

The data are presented in tabular form in Table I and plotted as a function of $\sin\theta/\lambda$ in Fig. 2. The γ values have been corrected as mentioned above. The p values are calculated allowing for the state of incomplete order in the crystal. The f values are defined by $f = p/p_0$, where p_0 is the scattering amplitude in the forward direction. For the three types of reflection, p_0 was obtained by normalizing the first three reflections to the calculated Fe spherical form factor of Weiss and Freeman,[3] which agreed very well with the measured Fe form factor. This procedure, which will be discussed more fully later, gives a good fit with the observed moment. For now, we wish to draw attention to the fact that as $\sin\theta/\lambda$ increases, the experimental points begin to deviate more widely from the smooth curve,

TABLE I. Observed magnetic scattering amplitudes and the form factor of Fe₃Al.

| h	k	l	$\sin\theta/\lambda$ (A^{-1})	γ	p (10^{-12} cm)	f
1	1	1	0.150	0.869 ± 0.010	0.477	0.816 ± 0.010
0	0	2	0.173	0.253 ± 0.003	0.135	0.765 ± 0.009
2	2	0	0.245	0.264 ± 0.002	0.851	0.600 ± 0.004
1	1	3	0.287	0.540 ± 0.004	0.297	0.507 ± 0.004
2	2	2	0.300	0.162 ± 0.002	0.087	0.494 ± 0.006
0	0	4	0.346	0.185 ± 0.002	0.596	0.420 ± 0.004
3	3	1	0.377	0.315 ± 0.002	0.175	0.299 ± 0.002
0	2	4	0.387	0.101 ± 0.001	0.054	0.307 ± 0.003
2	2	4	0.424	0.105 ± 0.001	0.338	0.238 ± 0.002
1	1	5	0.449	0.254 ± 0.002	0.141	0.241 ± 0.002
3	3	3		0.217 ± 0.001	0.119	0.203 ± 0.001
4	4	0	0.489	0.091 ± 0.002	0.293	0.207 ± 0.004
0	0	6	0.519	0.032 ± 0.001	0.017	0.097 ± 0.003
4	4	2		0.061 ± 0.002	0.034	0.193 ± 0.006
0	2	6	0.547	0.056 ± 0.002	0.179	0.126 ± 0.004
3	3	5	0.567	0.097 ± 0.001	0.054	0.092 ± 0.001
2	2	6	0.574	0.033 ± 0.001	0.018	0.102 ± 0.003
4	4	4	0.599	0.044 ± 0.004	0.141	0.099 ± 0.008
1	1	7	0.617	0.108 ± 0.001	0.060	0.102 ± 0.001
5	5	1		0.062 ± 0.002	0.035	0.060 ± 0.002
0	4	6	0.624	0.028 ± 0.002	0.015	0.085 ± 0.006
5	5	3	0.664	0.022 ± 0.002	0.012	0.020 ± 0.002
0	0	8	0.692	0.034 ± 0.003	0.109	0.077 ± 0.006
3	3	7	0.708	0.039 ± 0.002	0.022	0.038 ± 0.002
4	4	6	0.713	0.024 ± 0.002	0.013	0.074 ± 0.006
0	2	8		0.002 ± 0.002	0.001	0.006 ± 0.006
2	2	8	0.734	0.022 ± 0.002	0.071	0.050 ± 0.004
6	6	0		0.003 ± 0.002	0.009	0.006 ± 0.004
5	5	5	0.749	-0.002 ± 0.002	-0.001	-0.002 ± 0.002
6	6	2	0.754	0.018 ± 0.002	0.010	0.057 ± 0.006
0	4	8	0.774	0.006 ± 0.002	0.019	0.013 ± 0.004
1	1	9	0.788	0.052 ± 0.002	0.029	0.050 ± 0.002
6	6	4	0.811	-0.008 ± 0.004	-0.026	-0.018 ± 0.008
4	4	8	0.846	-0.002 ± 0.002	-0.006	-0.004 ± 0.004
3	3	9	0.861	0.011 ± 0.001	0.006	0.010 ± 0.001
5	5	7		-0.028 ± 0.002	-0.016	-0.027 ± 0.001
7	7	1		-0.011 ± 0.002	-0.006	-0.010 ± 0.002
0	0	10	0.865	-0.026 ± 0.002	-0.015	-0.085 ± 0.004
0	6	8		0.010 ± 0.001	0.005	0.028 ± 0.003
0	2	10	0.882	0.001 ± 0.002	0.003	0.002 ± 0.004
7	7	3	0.894	-0.029 ± 0.002	-0.017	-0.029 ± 0.002
2	2	10	0.899	-0.011 ± 0.001	-0.006	-0.034 ± 0.003
6	6	6		0.019 ± 0.002	0.010	0.057 ± 0.006
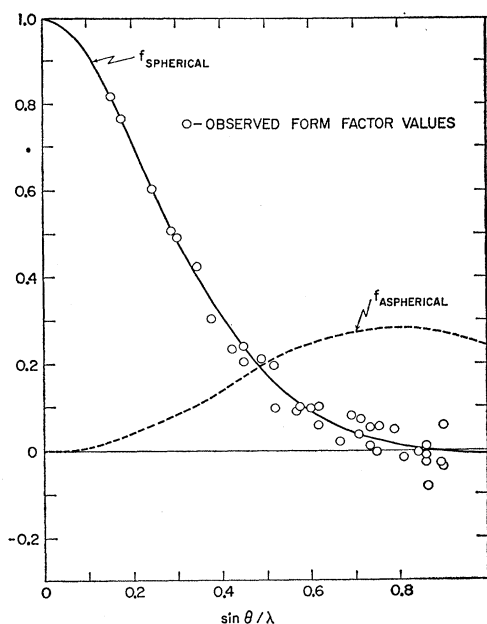
FIG. 2. The observed magnetic form-factor values of the (hhl) reflections of Fe₃Al as a function of $\sin\theta/\lambda$ in reciprocal angstrom units. The solid curve labeled $f_{\text{spherical}}$ is taken from Weiss and Freeman's calculation for Fe. The dashed $f_{\text{aspherical}}$ is the weighted average $(f_2-4f_1+3f_0)/5$ of their principal scattering factors. Deviations from the spherical curve should be proportional to this quantity multiplied by the appropriate asymmetry factor.

and at several places the form factor is, in fact, multi-valued or has a negative value. Quoted errors are the standard deviation of repeated measurements, averaged over all the accessible planes in the form.

3. Factors Affecting Accuracy of the Data

Besides the straightforward corrections mentioned previously, other experimental factors may prevent observation of the true scattering amplitude. These, together with a discussion of how they were treated in the present instance, are as follows.

(a) Primary and Secondary Extinction

Since the scattering power of the crystal under study depends upon the polarization state of the incident neutrons, the measured ratio must be corrected if extinction is present in the crystal. Extinction corrections based on calculation of integrated intensities are not applicable in our case, but we have been able to obtain practically extinction-free measurements in the following manner. Because we use a peak-height ratio method, secondary extinction can be investigated by missetting the Bragg angle (which reduces the number of coherently scattering blocks).[2] In this way we could show that none of the superlattice reflections suffered from extinction (as expected, since they are relatively weak) and could also find extinction-free ratios for the fundamental reflections. This latter point was confirmed

by comparison with the polycrystalline ratios measured for the first two strongest peaks. Measurements made at the shorter wavelength, by reducing the reflectivity, serve also as a test for the presence of primary extinction. In no case were changes noted upon changing wavelength from the polarization ratios measured as above. The values for γ listed in Table I are therefore considered to be free of extinction.

(b) Debye-Waller Temperature Correction

Again because this is a ratio method, the correction to the coherent intensity caused by thermal vibration of the atoms cancels for simple structures if the vibration amplitude of the d-shell electrons is the same as that of the nuclei. For the ordered Fe₃Al structure there exists a correction because of the differing Debye-Waller factors for Fe and Al atoms. This effect, although small, has been calculated using previously given quantities[12] and applied to the p values listed in Table I.

There remains the possibility of a difference in the Debye-Waller coefficient for the magnetic electrons and the nuclei. We investigated this point in the present case by noting whether a change in temperature affected the difference in the (600, 442) doublet, using a simple cryostat in which the crystal was in thermal contact with a liquid nitrogen reservoir. If temperature effects are important, one would expect some variation between 300° and 77°K. We find that, after correction for Brillouin saturation (as determined from an inner reflection) there is no change in the magnetic scattering amplitude of these two points within the experimental accuracy. We thus conclude that the fluctuation of the experimental points observed here is not a result either of possible asymmetric temperature factors or of different vibration amplitudes for electrons and nuclei.

(c) Multiple-Scattering Processes

The importance of considering the possibility of simultaneous reflection from more than one crystal plane when measuring weak structure factors has been emphasized by Renninger.[14] If another point in reciprocal space, besides the one under investigation, lies on the sphere of reflection, simultaneous reflection from this second plane may diminish the incident intensity intensity ("Aufhellung"). In addition, the reflected beam from the second point may serve as an incident beam and reflect back into the original direction through the reciprocal lattice vector that is the difference of the first two ("Umweganregung"). Finally, the inverse of this last process may serve to reduce the measured reflectivity. These effects, since they involve double reflection, are usually unimportant when intense reflections are being measured, but may become significant when either one or both of the other structure factors

[14] M. Renninger, Z. Physik 106, 141 (1937).

involved in the process are large compared to the one being measured. Only the first possibility applies in our case insofar as the weaker reflections are concerned, because a superlattice vector can be produced in the Fe₃Al reciprocal lattice only by combining a fundamental and a superlattice reciprocal vector.

Since the occurrence of these simultaneous reflections depends on accidental intersections of reciprocal lattice points with the sphere of reflection, they can, except in special cases, be altered by varying the wavelength (i.e., the radius of the sphere) or by changing the azimuth angle of the scattering normal (i.e., rotating the sphere about the reciprocal lattice vector). We have used both these methods of testing for the presence of double scattering in this study. The pairs of reflections (511, 333), (600, 442), and (551, 711) were examined both at $\lambda = 0.80$ and $\lambda = 1.05$ A. No change in any of the values outside experimental error would be detected. Secondly, the (600) and (442) polarization ratios were measured at a wavelength of 1.27 A while the crystal was rotated about the scattering normal, and again no change in scattering factor was measurable. We conclude that, at least for the superlattice reflections, the possible contribution to the scattered intensity from double scattering is not significant. This statement cannot be made with as much confidence concerning the fundamental reflections, because some small differences, outside experimental error, were observed in this case when rotating the crystal about the scattering normal.

IV. ANALYSIS OF THE DATA

Once these deviations from a smooth form-factor curve have been put on a firm experimental footing, we may analyze them for the information they contain about the spin density. In general, two methods are available: One may start with a given set of wave functions and the charge density constructed therefrom, perform a Fourier transformation, and compare the resulting set of scattering amplitudes with the observed data. Alternatively, the observed form factor may be inverted to give a Fourier projection of the density. The first procedure requires a specific model of the atom in the solid as a basis for choice of the wave functions; the latter is more difficult to free from experimental uncertainties, because the Fourier coefficients beyond the experimental cutoff in $\sin\theta/\lambda$ must be supplied by some approximation. It is, of course, true that once a theoretical form factor is found to fit a given set of data (as we shall find in the present case), no new information is obtained by the Fourier projection. Nevertheless, this procedure would be quite useful where a suitable specific model is lacking, and it is therefore instructive to determine with what confidence the method can actually be used, given present-day experimental techniques.

1. Comparison with Hartree-Fock Free-Atom Form Factors

It was mentioned earlier that the measured form factor of Fe₃Al agreed (at least in the small-angle region) with that of pure Fe, which is a not unreasonable result. The Fe form factor, in turn, was in surprising consonance with calculations[3],[15] made by using Hartree-Fock wave functions derived from a self-consistent field solution for the free iron atom in a configuration $3d^6 4s^2$. Arguments have been presented by Herring[16] to the effect that the radial charge distribution of the d electrons in the free atom and in the solid should not be much different; this is especially true of the unpaired electrons near the top of the band, whose wave functions, as the calculations of Stern[17] and Wood[8] show, have a localized, nearly atomic character. We accept here the spherical free-atom form factor of Weiss and Freeman as being a reasonably accurate representation of the radial dependence of the unpaired electrons in the iron atoms in Fe₃Al.

The deviations of the observed f values from this curve, and especially the different values obtained for reflections whose reciprocal lattice vectors have equal magnitude but different orientation, imply unequivocally that the unpaired spin density is not spherical. Therefore, we have attempted to fit our data with the Fe form-factor calculations that take into account the symmetry of the cubic crystalline field. Of the five-fold degenerate d-wave functions, the two e_g are those whose angular dependence shows maxima along the cubic [100] directions, the three t_{2g} along body-center [111] directions; a 2:3 proportion results in spherical symmetry, as in a half-full or completely full shell. The f values for solely e_g or t_{2g} symmetry were calculated for each reflection from the principal scattering factors given by Weiss and Freeman.[3] We then attempted to fit the observed value by some arbitrary but consistent proportion of the e_g and t_{2g} values.

This procedure allows a fairly consistent fit if one grants that the symmetry of the two iron atoms, Fe(I) and Fe(II), need not be the same. We find in particular that the (111) type, whose structure factor is proportional to the moment of Fe(I), represents a mixture of approximately 60% e_g – 40% t_{2g} symmetry, while the (200) type, proportional to the difference of twice the Fe(II) moment minus Fe(I), represents 10% e_g – 90% t_{2g}. The calculated values for the superlattice peaks can be seen to be in reasonable agreement with the experimental data in Figs. 3 and 4. The fundamental reflections, to be consistent with the above assignments, should correspond to 53% e_g. The agreement with the observed values is not so good in this case, although the average value for all the reflections is close to this figure. In particular, (440) and (444) lie significantly above

[15] J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957).
[16] C. Herring, J. Appl. Phys. **31**, 38 (1960).
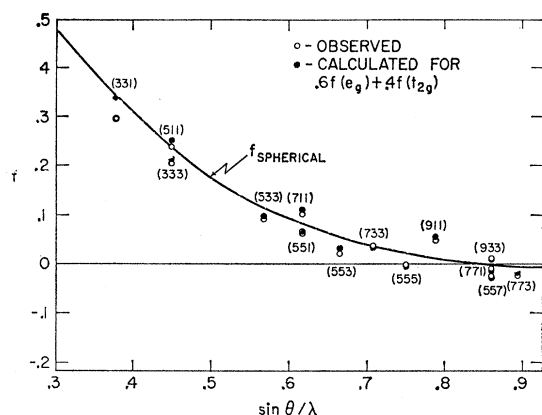[17] F. Stern, Phys. Rev. **116**, 1399 (1959).

FIG. 3. Comparison of the measured (111) type superlattice form factor with calculated values. The solid curve is the spherical form factor as in Fig. 2.

the calculated values, while (224) and (620) fall below. The explanation for these discrepancies must almost certainly be sought in double Bragg scattering, as already alluded to. The correct magnitude and direction of the expected change in the polarization ratio can be determined only by the knowledge of the exact scattering processes in each case.

In interpreting Figs. 3 and 4, it is important to recognize the restrictions implied by our procedure. First, the calculations were made assuming a common radial wave function for both e_g and t_{2g} electrons,[3] and in fitting our points we have not allowed for the possibility of a different spherical form factor (i.e., radial wave function) for the two iron types. Secondly, the wave functions were calculated according to the restricted Hartree-Fock method, which does not take into account the different exchange interaction for spins aligned parallel and antiparallel to the net spin of the atom.[15,18] Inclusion of these effects may give better
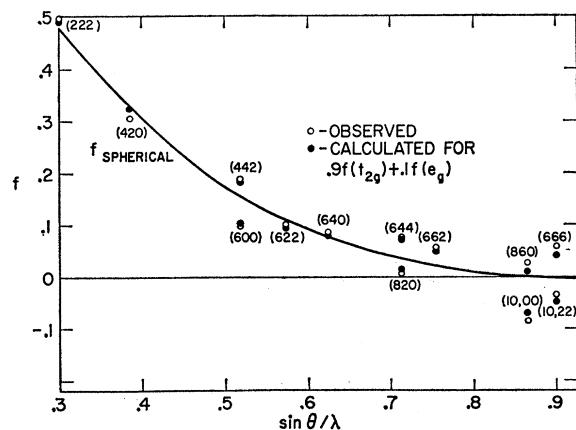

FIG. 4. Comparison of the measured (200) type superlattice form factor with calculated values.

[18] R. E. Watson and A. J. Freeman, Phys. Rev. 120, 1125 (1960); ibid. 120, 1134 (1960).

detailed agreement, but the systematic fit observed here gives some confidence that no substantial change would have to be made. Finally, the measurements represent scattering only from the unpaired electrons; hence, no detailed information can be obtained about the total d-electron density. With these qualifications, our analysis indicates that the unpaired electrons about the Fe(I) atom preferentially occupy e_g orbitals (60%), while those about Fe(II) slightly favor t_{2g} symmetry (52%) and are thus closer to being spherically symmetric. The fact that (200) type reflections are difference peaks is responsible for the departures of these structure factors from spherical symmetry.

We wish to comment here on the assumption made in the calculation of the structure factors that the two Fe(II) atoms are equivalent. A difference between these two atoms, related to their bonding with either near-neighbor Al or Fe(I) atoms, is of course possible.[5] Invoking such a model adds a contribution proportional to this difference to the (111) type reflections, so that some deviations would then be observed in both types of reflections even if the Fe(I) atom is spherical. There is no straightforward way of ruling out this possibility, but we can argue that the effect, if present, is small. This argument rests on the grounds that the moment and symmetry of the Fe(I) atom and the pure Fe are doubtlessly related, so that a model predicting spherical symmetry for the Fe(I) atom is less likely, in view of the finding in pure Fe of a preference for e_g symmetry.[3] In either case, the most important conclusion, asphericity of the charge density in the unit cell, would not be altered.

2. Fourier Inversion of the Data

Because the divergences in our observed data from a spherical model are so noticeable, we tried to find what features of the magnetic charge density can be recognized in two-dimensional Fourier projections. The major difficulty facing this effort is the finite termination of the Fourier series caused by the lack of data beyond the experimental limit in $\sin\theta/\lambda$. However, because the unpaired electrons seen by the neutron are (predominantly) in d shells and not in the atom core, the form factor falls off more rapidly than the x-ray scattering factor, so the situation is less serious than if similar information were to be derived from x-ray measurements. Also, temperature motions not independent of the nuclei have been automatically corrected for and the phase of the magnetic amplitude, relative to the nuclear, is known unambiguously. We have chosen to obviate series termination errors by using difference projections of spherical and observed densities,[19] although other methods (e.g., artificial convergence factors) are also available.[20] This method relies on the

[19] R. Brill, Acta Cryst. 3, 333 (1950).
[20] J. Waser and V. Schomaker, Revs. Modern Phys. 25, 671 (1953).

assumption that in the Fourier difference sum

$$\Delta\rho(x,y) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \Delta F(h,k) \, \exp[-2\pi i)hx+ky)],$$

the terms $\Delta F = F_{observed} = F_{spherical}$ corresponding to higher values of h, k, than the observed limit will make a negligible net contribution. The effect on the density map of varying the cutoff point is the obvious criterion for judging the validity of this approximation.

The Fourier syntheses were performed on the IBM 704 using a program for centrosymmetric structures written by R. Sass.

(a). Bcc Fe

In order to illustrate more clearly the features of e_g and t_{2g} projected charge densities, we treated in addition to Fe₃Al the simpler case of bcc Fe, using the theoretical form factors of Weiss and Freeman[3] for both the spherical and aspherical cases. It was found that features of the e_g and t_{2g} lobes were easily recognizable in total projections carried out only to $\sin\theta/\lambda = 0.7$ A^{-1}. We present in Fig. 5 the difference projection ($\rho_{aspherical} - \rho_{spherical}$) on (110) for the cases of e_g and t_{2g} symmetry, carried out to $\sin\theta/\lambda = 1.2$ A^{-1}. Inspection of these maps shows that the net changes from the spherical density are quite well defined, the highest region corresponding to a density of about 1.5 $\mu_B/$A^2. Integration of the difference projection in Fig. 5(b) yields only $-5 \times 10^{-4} \, \mu_B/$atom, while integration over a total projection carried out to the same point shows that essentially all the charge of 2.20 $\mu_B/$atom has been recovered. Termination errors seem to have been reduced to the order of the shallow peaks seen between the atoms.

(b). Fe₃Al

We used the set of thirty-six structure amplitudes in the [110] zone to prepare difference projections ($\rho_{observed} - \rho_{spherical}$) on the (110) plane. Because data were collected to a limit lower than above ($\sin\theta/\lambda = 0.9$ A^{-1}) and because the observed data contain experimental uncertainties, this projection was studied in somewhat more detail. These results are illustrated in Fig. 6.

Figure 6(a) identifies the portion of the (110) plane covered by the synthesis, the smallest asymmetric unit, which is one-sixteenth the total area. Figures 6(b), (c), and (d) show the effect on the map of varying the cutoff point through $\sin\theta/\lambda = 0.7$, 0.8, and 0.9 A^{-1}, respectively. The regions of positive and negative density sharpen up considerably as the limit is increased. Since the
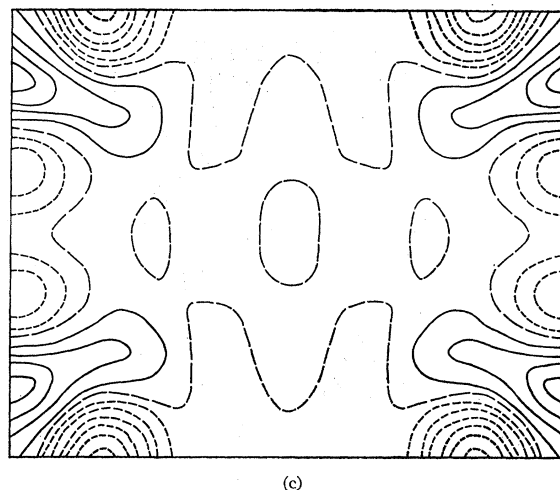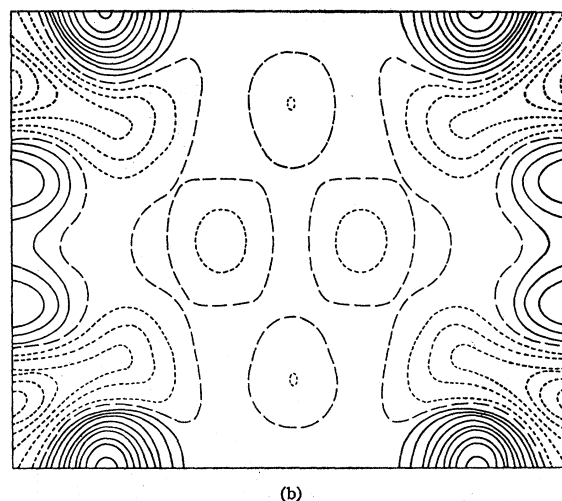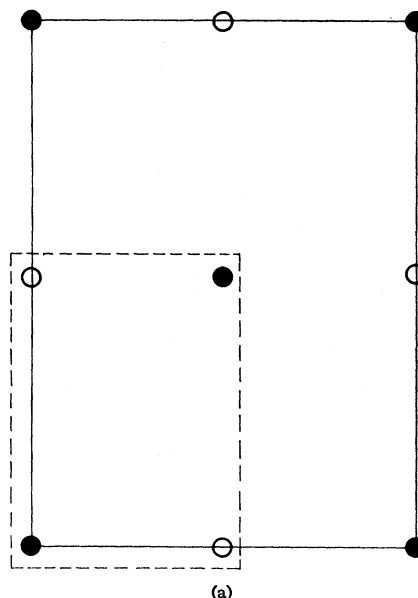

(a)

(b)

(c)

FIG. 5. Difference projections $\rho_{aspherical} - \rho_{spherical}$ on the (110) plane of bcc Fe prepared from theoretical form factors. (a) (in dashed outline) shows the portion of the plane covered by the projections; the atoms shown as open circles project from $a/\sqrt{2}$ away. (b) shows the $\Delta\rho$ for e_g symmetry, (c) for t_{2g} symmetry. Contours are plotted at intervals of 0.152$\mu_B/$A^2. Zero contours are shown as dashed lines, positive as solid lines, and negative as dotted lines.

approximation must become better as more data are included, we believe these aspects represent features of the difference density that are relatively free of termination errors. Integration of the total and difference

projections for $\sin\theta/\lambda \leq 0.9 \, A^{-1}$ reinforces this conclusion: the former yields $1.35 \, \mu_B$/atom versus an expected 1.32, the latter $-0.003 \, \mu_B$/atom. The differences are now shallower than in the case of bcc Fe, the

Fe (I)

Al

Fe (II)

(a)

(b)

(c)

(d)

(e)
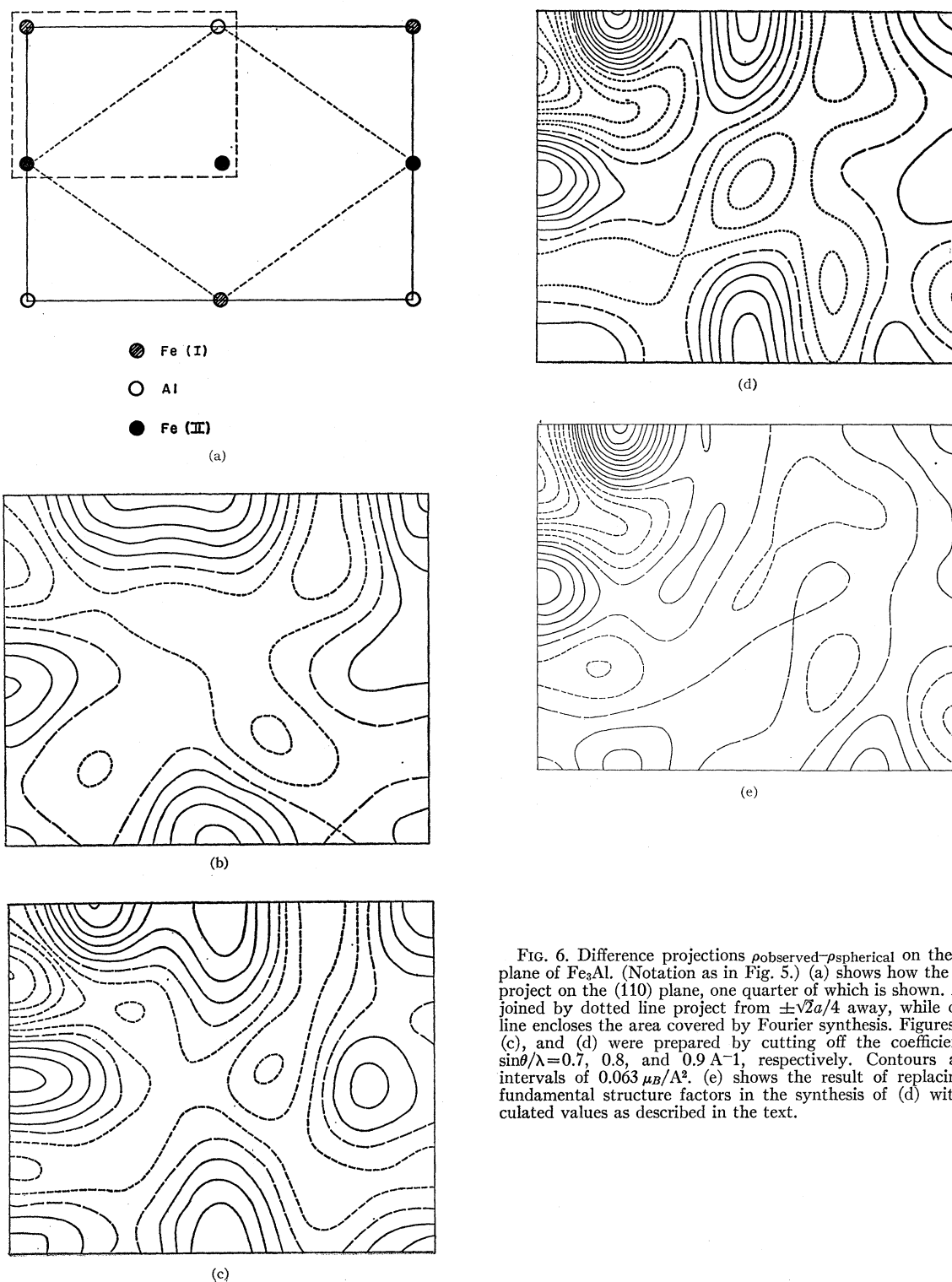
FIG. 6. Difference projections $\rho_{observed} - \rho_{spherical}$ on the (110) plane of Fe_3Al. (Notation as in Fig. 5.) (a) shows how the atoms project on the (110) plane, one quarter of which is shown. Atoms joined by dotted line project from $\pm\sqrt{2}a/4$ away, while dashed line encloses the area covered by Fourier synthesis. Figures 6(b), (c), and (d) were prepared by cutting off the coefficients at $\sin\theta/\lambda = 0.7$, 0.8, and 0.9 A^{-1}, respectively. Contours are at intervals of $0.063 \, \mu_B/A^2$. (e) shows the result of replacing the fundamental structure factors in the synthesis of (d) with calculated values as described in the text.

highest peak corresponding to a density of about 0.57 μ_B/A^2.

Because of the earlier mentioned possibility of errors in the fundamental structure factors due to double Bragg scattering, the synthesis was repeated with calculated values for these reflections consistent with the symmetry observed for the superlattice reflections. This result is depicted in Fig. 6(e). Several quantitative, but not qualitative, changes have taken place, particularly in the region between the atoms. The principal result has been to shift some of the positive density from the midpoints between Fe(I) and Al and between the two Fe(II) closer to the Fe atoms. The configuration about Fe(I) has sharpened in detail, the peak density now being 0.65 μ_B/A^2.

This last synthesis, Fig. 6(e), represents the most reliable picture of the aspherical electron density derived to data, inasmuch as termination errors and experimental uncertainties have been removed in the best possible manner presently available. The most noticeable features are in the area about Fe(I) which, by comparison with Fig. 5(b), shows characteristics of e_g symmetry. This result and the fact that only slight densities are seen around Fe(II) were, of course, expected from the form-factor analysis. The differences between Fig. 6(e) and (d) point up the necessity of having accurate data if spurious detail in the density map is to be avoided. One may question, finally, how sensitive the appearance of these maps is to the choice of the spherical form factor. Granted that the consistent fit between observed and calculated form factors is enough justification for the choice made in the present instance, the null result obtained by integration of the difference charge densities would seem to be a valuable criterion for a choice in a case where the appropriate spherical form factor is uncertain.

V. DISCUSSION AND CONCLUSIONS

The results presented here are of interest in relation to the question of electron sharing in the Fe—Al bond in the alloy Fe₃Al, but in their broader aspects they also have some bearing on the electronic structure of elements of the first transition period.

With regard to the first point, electron transfer had been suggested by Nathans et al.[10] as the origin of the lower moment on the Fe(II) atom. Later, Sato and Arrott[21] attributed this result to a different Brillouin temperature dependence of the Fe(II) sublattices, while Goodenough[5] suggested that some of the Fe(II) spins are antiferromagnetically aligned. We believe that the finding of different symmetry for the unpaired spin density of the two iron atoms definitely points to some intrinsic change in the number or nature of the $3d$

electrons in Fe(II) by reason of the near-neighbor bond with Al. This conclusion is further borne out by neutron diffraction measurements[22] on Fe—Al alloys of concentration 33–50 at. % Al, which exhibit no long-range antiferromagnetic order at 4.2°K but an Fe moment greatly reduced from 2.2 μ_B, as determined from the paramagnetic scattering. It is interesting to note that the change of symmetry from Fe(I) to Fe(II) can be correlated with the change in moment; that is, if 0.7 unpaired e_g electrons are removed from Fe(I), the resulting symmetry is very close to that observed in Fe(II).

More generally, we believe that the present study unambiguously demonstrates that aspherical d-electron charge densities exist in Fe series elements, of sufficient magnitude to be visible in two-dimensional Fourier projections when difference syntheses are used. It has proved possible in the present instance to obtain agreement with experiment by means of a relatively unsophisticated model of the Fe atom, which does not relax any of the constraints of the restricted Hartree-Fock method. In terms of a band model, as noted earlier, the unpaired spin density seen by the neutrons comes from electrons of higher energy whose wave functions are sharpened up not only in their radial but also in their angular dependence.[17] The observed admixtures of e_g and t_{2g} symmetry are thus to be related to the way in which these levels are filled up in the actual band structure of the solid, and are in no way inconsistent with the calculations indicating that crystal field effects in metals are much smaller than the total d bandwidth. An exact prediction of the expected symmetry of the unpaired spin density requires accurate knowledge of the band structure, including exchange splitting in the ferromagnetic state, and of the density-of-states curve. Qualitatively, however, the change in moment and symmetry of Fe(II) referred to above is consistent with a band structure in the alloy with the t_{2g} levels lying below[5] the e_g, if the band for the Fe(II) sublattice is displaced in such a way as to shift the Fermi level toward the bottom of the band and at the same time toward a lower density of states. Although a more quantitative comparison with theory for this case is not possible at present, it is clear that polarized neutron measurements of the type reported here contain the necessary information if such correlations are to be made in the future.

[21] H. Sato and A. Arrott, J. Appl. Phys. 29, 515 (1958).

[22] R. Nathans and S. J. Pickart (unpublished).