REVIEWS OF MODERN PHYSICS VOLUME 25, NUMBER 1 JANUARY, 1953

Neutron Diffraction Studies of Zinc Ferrite and Nickel Ferrite*

J. M. HASTINGS AND L. M. CORLISS

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York

The chemical and magnetic structures of zinc ferrite and nickel ferrite have been investigated at room temperature by means of neutron diffraction. In agreement with previous x-ray investigations zinc ferrite has been found to possess a completely regular spinel structure with an oxygen parameter of 0.385±0.002. The diffraction peaks show no evidence of coherent magnetic scattering, whereas the background exhibits normal paramagnetic diffuse scattering. This eliminates the possibility of an antiferromagnetic structure at room temperature. In the case of nickel ferrite, calculated intensities based upon an inverted structure and the Néel model of ferrimagnetism are in good agreement with the observed intensities.

INTRODUCTION

THE crystal structure of ferrites has been the subject of several investigations in recent years.[1,2] Aside from questions of technology, considerable interest derives from the explanation of their interesting magnetic properties given by Néel.[3] The saturation moment, according to the theory of Néel, is related in a simple and elegant manner to the distribution of magnetic ions among the available lattice sites. However, the precise location of the various cations by means of x-rays presents a difficult problem in many cases of interest because of the similarity in scattering power of the iron group elements. Neutron diffraction as a tool for studying the ferrite problem offers not only the means of distinguishing between the various members of the iron group but also a means of determining the location, magnitude, and relative orientation of atomic moments.

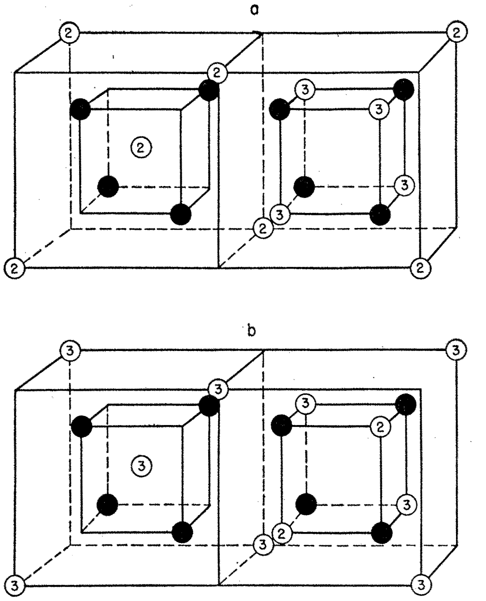

FIG. 1. (a) Two octants of the regular spinel structure. Open circles with numbers refer to di- and tri-valent cations. Solid circles refer to oxygen anions. (b) Same for inverted spinel.

CRYSTAL STRUCTURE

Nickel and zinc ferrite belong to a large class of compounds having the general formula $X^{+2}Y_2^{+3}O_4$ and crystallizing with the spinel structure. The unit cell is cubic with a cell edge of approximately 8.4A and contains eight molecules. The structure can be described as a close-packed assemblage of oxygen atoms with metal atoms occupying positions in some of the interstices. The metal positions are of two types: those in which the oxygen atoms are tetrahedrally coordinated

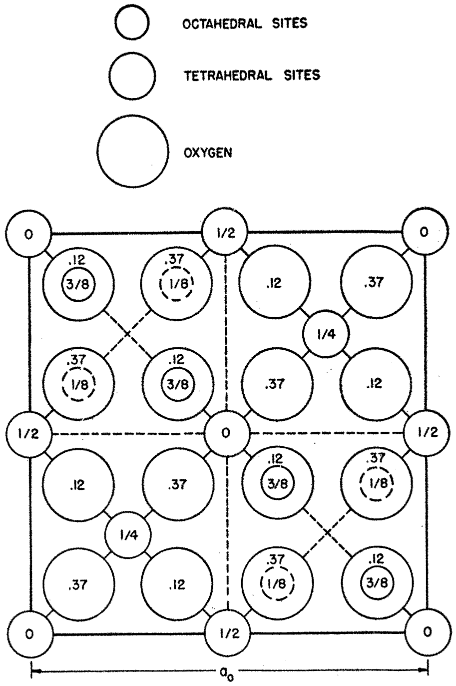

FIG. 2. Projection on a cube face of lower half of spinel unit cell (after Wyckoff).

---

* Research carried out under the auspices of the U. S. Atomic Energy Commission.

[1] E. J. W. Verwey and E. L. Heilmann, J. Chem. Phys. **15**, 174 (1947).

[2] E. F. Bertaut, J. phys. et radium **12**, 252 (1951).

[3] L. Néel, Ann. phys. **3**, 139 (1948).

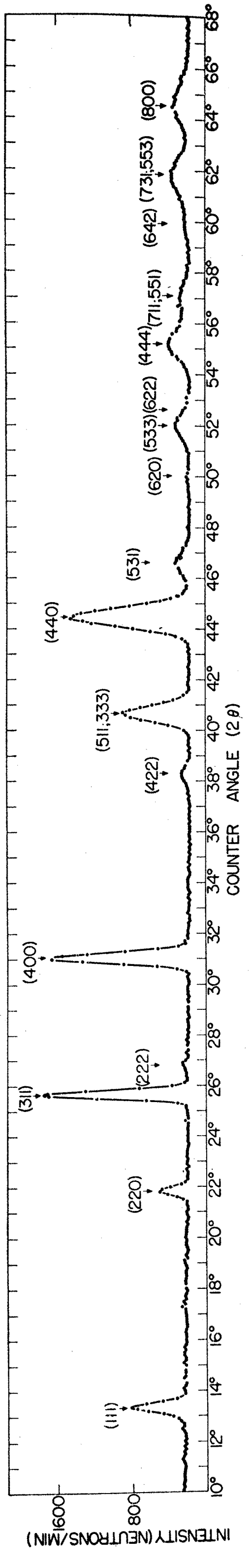

Fig. 3. Neutron diffraction pattern of $ZnFe_2O_4$.

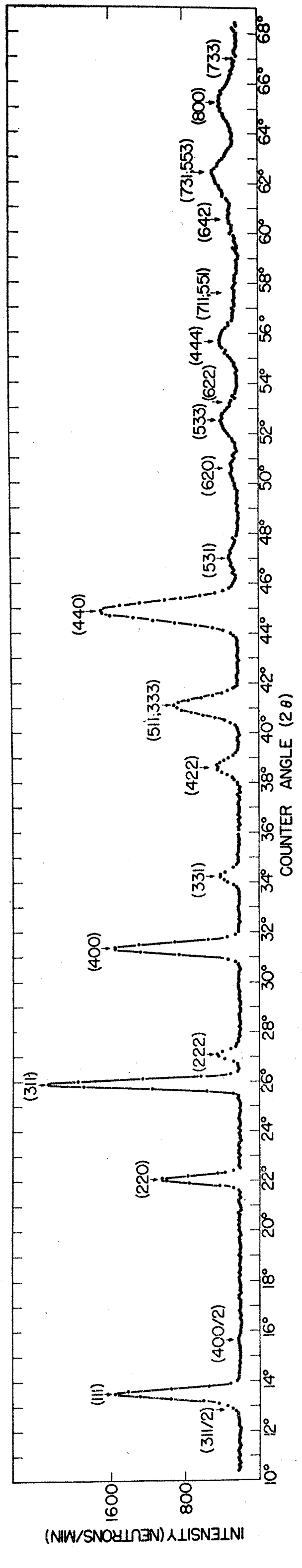

Fig. 4. Neutron diffraction pattern of $NiFe_4O_2$.

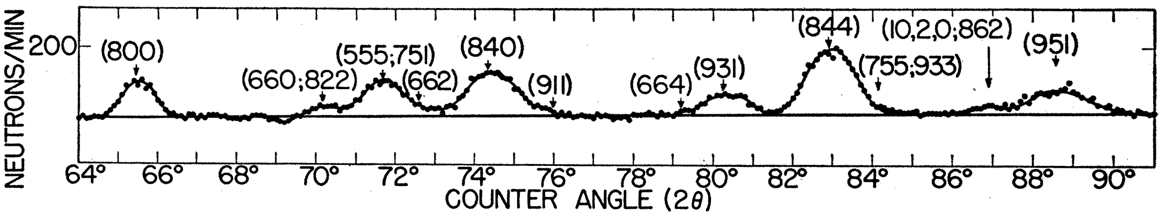

FIG. 5. Neutron diffraction pattern of $NiFe_2O_4$ with improved resolution.

to the metal atom, and those in which the surrounding oxygen atoms have octahedral symmetry. Of the twenty-four positions available to the metal atoms in the unit cell, eight are of the tetrahedral type and sixteen belong to the octahedral category. One obvious way to meet the symmetry requirements would be to place the sixteen trivalent ions in the sixteen octahedral positions and the eight divalent ions in the eight tetrahedral positions. It was shown by Barth and Posnjak[4] that another arrangement, which they have termed an "equipoint" structure, is also possible. According to this scheme, the sixteen trivalent ions occupy all of the tetrahedral sites and half the octahedral sites taken at random, while the divalent ions fill the remaining octahedral positions. The first arrangement in which each cation species occupies only one type of site is commonly referred to as "regular" or "normal," whereas the "equipoint" structure has been given the designation "inverted" or "inverse." It is also conceivable that cases will arise that are intermediate between these two extremes. In Fig. 1 are shown two octants of the spinel unit cell for both the inverted and regular arrangements. Figure 2, taken from Wyckoff,[5] is a projection on a cube face of the atoms in the lower half of the unit cell.

Verwey and Heilmann[1] have investigated a large number of spinels from both a theoretical and experimental point of view. On the basis of electrostatic considerations, they conclude that the regular arrangement should be more stable than the inverted one, in compounds of the type $X^{+2}Y_2^{+3}O_4$. They report that x-ray studies confirm the prediction for the cases of $ZnFe_2O_4$ and $CdFe_2O_4$ but not for $CuFe_2O_4$ and $MgFe_2O_4$. Furthermore, they show empirically by a consideration of the variation of lattice constant with the divalent ion radius that the ferrites of Mn^{++}, Fe^{++}, Co^{++}, and Ni^{++} may also be inverted. More recently Bertaut,[2] working in the region of anomalous x-ray dispersion, has concluded that zinc ferrite is regular and nickel ferrite inverted, while the ferrites of magnesium and copper are partially inverted to an extent which depends on the conditions of preparation.

TABLE I. Coherent scattering amplitude$\times 10^{12}$ cm.

	Nuclear	Magnetic
O^{-2}	0.58	...
Fe^{+3}	0.96	1.35f
Ni^{+2}	1.03	0.54f
Zn^{+2}	0.59	...

THE NÉEL MODEL

According to the Néel model of ferrimagnetism,[3] the exchange integrals between an arbitrary pair of metal ions is such as to produce an antiparallel alignment of the two. The octahedral-tetrahedral coupling, however, is taken to be considerably stronger than that between ions located on the same type of crystallographic site. Thus, the spins of ions in the octahedral positions are coupled parallel to one another and at the same time antiparallel to those of the tetrahedral ions. In an inverted spinel the saturation moment is then determined solely by the atomic moment of the divalent cation. In zinc ferrite where only the weak octahedral-octahedral coupling can be of importance, one would anticipate paramagnetic or at most antiferromagnetic behavior. A neutron diffraction study of Fe_3O_4 has been recently reported by Shull, Wollan, and Koehler,[6] and it confirms both the inverted structure and the Néel coupling scheme. In the present paper neutron diffraction data on both $ZnFe_2O_4$ and $NiFe_2O_4$ will be presented. Work on other ferrites is in progress and will be reported in the near future.

EXPERIMENTAL

The neutron diffraction apparatus and technique used in the present experiments are very similar to those of Shull, Wollan, and co-workers.[7] A heterochromatic beam of neutrons emerging from the reactor is made to strike a lead single crystal oriented on a spectrometer table set to diffract 1.125A neutrons. The reflected beam passes over a second spectrometer table upon which the powder sample is placed. The monochromatic beam is diffracted into a series of Debye halos which are scanned automatically by rotation of a BF_3 detector about the axis of the specimen. The chief innovation of the present apparatus is the use of Soller slits and wide beams to obtain improved resolution without too great a sacrifice in intensity.

The samples of zinc ferrite and nickel ferrite used in the present investigation were very kindly prepared by Dr. V. C. Wilson at the General Electric Research

---

[4] T. F. W. Barth and E. Posnjak, Z. Krist. **82**, 325 (1932).

[5] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951).

[6] Shull, Wollan, and Koehler, Phys. Rev. **84**, 912 (1951).

[7] E. O. Wollan and C. G. Shull, Phys. Rev. **73**, 822 (1948).

Laboratory. The specimens were examined in the form of 325 mesh powders, contained in flat cells $\frac{1}{2}$ in.×$2\frac{1}{2}$ in. ×4 in. in size, and as sintered blocks having about the same dimensions and about 0.9 the theoretical density. Different preparations were found to agree to within the precision of measurement on any one sample.

Diffraction patterns obtained with these materials are shown in Figs. 3, 4, and 5. The last of these patterns was taken under conditions of somewhat improved resolution.

METHOD OF CALCULATION

The integrated power P_{hkl} of a diffraction peak obtained in transmission through a flat cell is computed from the expression

$$P_{hkl}=(P_0\lambda^3 l/4\pi r)(N^2h\rho'/\rho)(e^{-\mu h \sec\theta}/\sin^2 2\theta)J_{hkl}F_{hkl}^2. \quad (1)$$

TABLE II. A comparison of observed intensities with those calculated for a regular structure for $ZnFe_2O_4$. Absolute units (neutrons/min) are used, based upon nickel as a standard.

hkl	Calculated	Observed
(111)	1900	1900
(220)	727	757
(311)	4820	4840
(222)	166	144
(400)	5890	6320
(331)	52	0
(422)	375	325
(511); (333)	3940	4100
(440)	9820	10300
(531)	900	1035
(620)	172	100
(533) (622)	1210	1190
(444)	2340	2300
(711); (551)	1030	1205
(642) (731); (553)	2620	2720
(800)	2260	2360

The first term is an instrumental constant in which P_0 is the number of neutrons striking the sample in unit time, λ the wavelength, l the counter slit height, and r the distance from the counter slit to the sample. The second term, which is a constant for a given specimen contains N the number of unit cells per unit volume, h the nominal thickness of the sample, ρ' the apparent density of the powder, and ρ the density of the solid. In the third term, θ is the Bragg angle, and μ is the effective linear absorption coefficient determined by measurement of the actual transmission of the sample $e^{-\mu h}$. J_{hkl} is the multiplicity, and F_{hkl} is the structure factor for the (hkl) reflection. In the case of scattering of unpolarized neutrons both by nuclei and by aligned atomic spins, Halpern and Johnson[8] have shown that the structure factor is given by

$$F^2=F_{\mathrm{nuc}}^2+q^2F_{\mathrm{mag}}^2, \quad (2)$$

where F_{nuc}^2 is the structure factor for nuclear scattering alone and F_{mag}^2 is the structure factor for magnetic scattering. If **e** is a unit vector parallel to the scattering vector (in this case, the normal to the set of diffracting planes) and **κ** is a unit vector in the direction of magnetization, then the quantity q^2 is given by

$$q^2=1-(\mathbf{e}\cdot\boldsymbol{\kappa})^2=\sin^2(\mathbf{e},\boldsymbol{\kappa}). \quad (3)$$

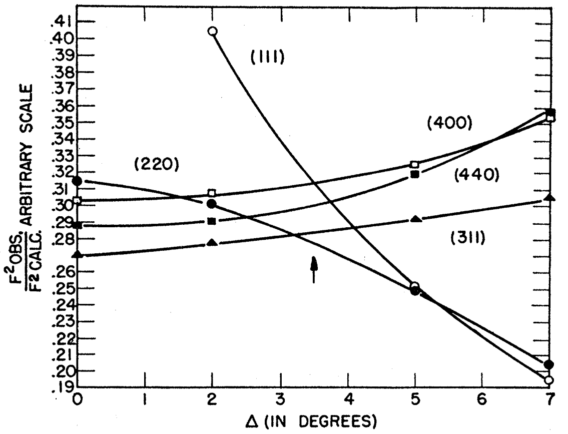

FIG. 6. The ratio $F_{\mathrm{obs}}{}^2/F_{\mathrm{calc}}{}^2$ for $ZnFe_2O_4$ plotted as a function of the parameter Δ, which describes the oxygen positions in the lattice.

The magnetic atomic scattering amplitude to be used in the computation of F_{mag}^2 is given by the expression

$$D=\frac{e^2}{mc^2}\gamma Sf=0.539\times10^{-12}Sf\ \mathrm{cm}, \quad (4)$$

where S is the electronic spin quantum number of the scattering atom, e and m are the charge and mass of the electron, γ is the magnetic moment of the neutron in nuclear magnetons, and f is the form factor for the magnetic electrons. Halpern and Johnson have also shown that for the case of an ideal paramagnetic substance the magnetic scattering will be entirely incoherent. The differential cross section for magnetic scattering into solid angle $d\Omega$ is given by

$$d\sigma_m=\tfrac{2}{3}S(S+1)(e^2\gamma/mc^2)^2f^2d\Omega, \quad (5)$$

where all the symbols have the same meaning as in (4). The above equations and their experimental implications have been discussed at length by Shull and co-workers[6,9] in connection with their extensive investigations of the scattering of neutrons by magnetic materials. The coherent scattering amplitudes used in the present calculations are listed in Table I. The nuclear amplitudes are taken from the tabulation of Shull and Wollan,[10] and the magnetic amplitudes are computed from Eq. (4).

The diffraction pattern of $ZnFe_2O_4$ shown in Fig. 3 can be interpreted quantitatively in terms of a regular spinel structure, with no coherent magnetic contribution. Table II lists the calculated integrated intensities

---

[8] O. Halpern and M. H. Johnson, Phys. Rev. **55**, 898 (1939).

[9] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

[10] C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

TABLE III. Comparison of calculated and observed integrated intensities for $NiFe_2O_4$ for inverted form using Néel scheme of magnetic coupling. Absolute units (neutrons/minute) are used.

hkl	Nuclear	Calculated magnetic	Total	Observed
(111)	730	6020	6750	6470
(220)	2010	1270	3280	3270
(311)	8490	0	8490	8550
(222)	93	893	986	1110
(400)	5880	1210	7090	7270
(331)	2	1207	1210	1170
(422)	1280	380	1660	1700
(511); (333)	5530	0	5530	5790
(440)	14450	15	15440	15620
(531)	370	600		
(620)	730	105	3150	3280
(533)	2115	0		
(622)	55	145		
(444)	2530	105	3180	3040
(711); (551)	385	155		
(642)	1195	45	5390	5280
(731); (553)	4150	0		
(800)	3530	0	3550	3390
(733)	20	0		
(660); (822)	705	0	3920	4120
(751); (555)	3170	0		
(662)	40	0		
(840)	4420	0	4650	4710
(911)	230	0		

based on this structure together with the corresponding observed intensities. The data have been put on an absolute basis by comparison with a nickel standard having a coherent scattering cross section of 13.4 barns. The Debye-Waller temperature factor was obtained in the usual way from a plot of $F_{\text{calc}}^2/F_{\text{obs}}^2$ against $\sin^2\theta/\lambda^2$. The positions of the oxygen atoms in the spinel structure are fixed by a parameter u, which is in the neighborhood of $\frac{3}{8}$. If u is exactly $\frac{3}{8}$, the oxygen atoms form a cubic close-packed array. A u parameter greater than this value implies a contraction of the oxygen lattice about the octahedrally coordinated metal atoms and a corresponding expansion about the tetrahedrally coordinated ones. Figure 6 shows a plot of $F_{\text{calc}}^2/F_{\text{obs}}^2$ *versus* the deviation Δ of this parameter, expressed in angular measure from the value $\frac{3}{8}$ $[u=(135°+\Delta)/360°]$. A value of $\Delta=3.5°$ or $u=0.385$ was used. The calculated intensities are sufficiently sensitive to this parameter, as well as to partial inversion, to permit a determination of Δ to $\pm 0.7°$ or u to ± 0.002. An upper limit of 5 percent can be set on the amount of possible inversion.

An examination of the diffraction pattern of $ZnFe_2O_4$ shows a sloping background at low angles characteristic of paramagnetic diffuse scattering. The diffuse scattering cross section has been measured as a function of angle, and the extrapolated value for unit form factor is equal to 3.5 ± 0.3 barns/steradian/molecule. The calculated cross section for a paramagnetic arrangement of the ferric ions in the octahedral positions is 3.39 barns/steradian/molecule. This agreement together with the fit obtained in the absolute intensities of the Bragg reflections in which only nuclear scattering was considered leads to the conclusion that there is no octahedral-octahedral magnetic coupling at room temperature. It should be emphasized that antiferromagnetic coupling of the Fe^{+3} ions on the octahedral sites would lead to a coherent magnetic contribution to the diffraction pattern comparable in magnitude with that of the nuclear scattering, thereby completely spoiling the agreement in Table II.

The interpretation of the $NiFe_2O_4$ data involves an additional consideration, namely, the coherent magnetic scattering. The "chemical" structure, as distinct from the "magnetic" structure, can in principle be determined from the outer Bragg peaks which have no magnetic contributions because of the form factor fall-off. However, the nuclear scattering amplitudes of nickel and iron differ by only seven percent, so that these peaks are insensitive to the degree of inversion. The magnetic contributions, on the other hand, are strongly dependent on the model. If one assumes a completely inverted structure and the Néel scheme of antiferromagnetic coupling between octahedral and tetrahedral sites, satisfactory agreement with experiment is obtained as is shown in Table III. The magnetic scattering has been corrected assuming a g factor[11] for Ni^{++} of 2.3 and a saturation magnetization[12] at room temperature equal to 0.9 times the value at absolute zero. As in the case of $ZnFe_2O_4$, a Debye-Waller temperature correction and a u parameter were determined. Figure 7 shows a plot of $F_{\text{calc}}^2/F_{\text{obs}}^2$ *versus* $\sin^2\theta/\lambda^2$ which was used to obtain the effective Debye temperature of $NiFe_2O_4$. The u parameter was determined in the same manner as for the zinc compound and has the value 0.381 ± 0.003.

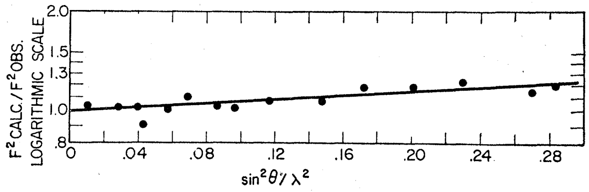

FIG. 7. Ratio of calculated to observed structure factors for diffraction peaks of $NiFe_2O_4$ plotted against $\sin^2\theta/\lambda^2$.

In order to fit the calculated intensities to the observed, it is necessary to assume a form factor, shown in Fig. 8, describing the angular dependence of the magnetic scattering amplitude. In the case of $NiFe_2O_4$ the form factor cannot be obtained by independent means but can be justified by the following considerations. The curve shown in Fig. 8 is smooth and can be made to extrapolate, as it should, to unity at zero scattering angle. The use of an incorrect model to calculate not only the relative peak intensities but also the absolute intensities of Table III would, in general, require a form factor curve of irregular shape. The curve of Fig. 8 is similar to that obtained by Shull, Strauser, and Wollan[9] for Mn^{++} in the compounds MnF_2 and MnO.

---

[11] H. G. Beljers and D. Polder, Nature **165**, 800 (1950).

[12] R. Pauthenet and L. Bochirol, J. phys. et radium **12**, 249 (1951).

In fact, the intensities computed using the Mn^{++} form factor agree moderately well with those observed for $NiFe_2O_4$. While it is not unreasonable to expect the form factor to resemble that for Mn^{++}, it should be remembered that the curve for nickel ferrite is a rather complicated average involving two ionic species and two different crystallographic sites. A radial distribution of the magnetic electrons is obtained in a formal way by inverting the form factor curve. Such a distribution, which of course can have only qualitative theoretical significance, is shown in Fig. 9.

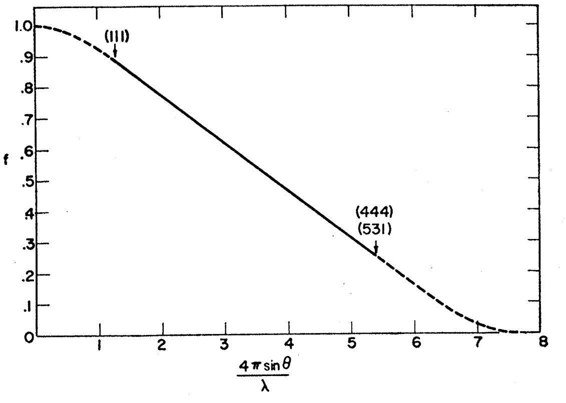

FIG. 8. Magnetic amplitude form factor for $NiFe_2O_4$ obtained from Bragg reflections.

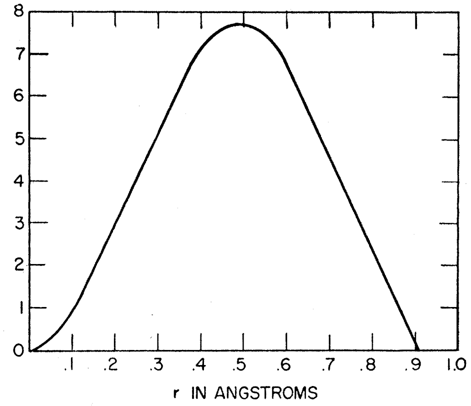

FIG. 9. Radial distribution of "3d" electrons in $NiFe_2O_4$ obtained from inversion of form factor in Fig. 8.

Although the fit obtained using the Néel model is not necessarily unique, certain other structures consistent with the saturation moment can be unambiguously eliminated by the diffraction data. For example, a completely regular structure containing ferromagnetically coupled Ni^{++} ions on tetrahedral sites, and either paramagnetic or antiferromagnetically coupled Fe^{+++} ions on octahedral sites would result in a (111) intensity which is lower than the observed by a factor of about 20. An inverted arrangement in which the Fe^{+++} ions are paramagnetic is likewise eliminated by the data. On the other hand, assuming the Nèel model, the computed intensities are not sensitive to incomplete inversion. The data require nickel ferrite to be at least 80 percent inverted, i.e., 80 percent of the nickel ions must occupy tetrahedral sites. If, however, the departure from the ideally inverted structure were as great as this, the saturation moment as calculated by Néel's method would be grossly in error. The possibility of ordering the Fe^{+++} and Ni^{++} ions on octahedral sites according to the scheme proposed by Verwey, Haayman, and Romeijn[13] for Fe_3O_4 at low temperatures has also been considered. Calculations show the effect to be too small to be observable with a powdered sample.

---

[13] Verwey, Haayman, and Romeijn, J. Chem. Phys. **15**, 181 (1947).

DISCUSSION

C. KITTEL, *University of California, Berkeley, California:* We can estimate the Néel temperature for zinc ferrite by extrapolating experimental measurements of the Curie temperatures of Mn-Zn and Ni-Zn ferrites. In this way we find $T_c = 150 \pm 50$°K, so that Hastings and Corliss should not have expected order in zinc ferrite at room temperature. Neutron work at liquid air temperature is indicated.

C. P. GUILLAUD, *Centre National de la Recherche Scientifique, Bellevue, France:* We pointed out for the first time that atoms located in different crystallographic planes could give rise to a kind of antiferromagnetism, which afterward Néel called ferrimagnetism. In the definite compound Mn_2Sb,[1] we distinguished between manganese Mn_I atoms located in the (001) planes and manganese Mn_{II} atoms not located in the basic planes (Fig. 1). In order to interpret the saturation moment, we advanced the hypothesis that the Mn_I atoms are in the $3d^5$, $4s^2$ state and the Mn_{II} atoms in the $3d^7$ state, the moments of spin of these two groups of atoms being antiparallel. In support of this hypothesis, we had considered the paramagnetic properties, the curvature of the curve $1/\chi = f(T)$ being explained by the existence of two different values of the molecular field. This hypothesis was likewise supported by the spontaneous magnetization curve $\sigma/\sigma_0 = f(T/\theta)$, by the empirical laws of Hume-Rothery and by the distance of 2.70A between Mn_I and Mn_{II} which gives rise to negative interactions.

In the course of our work, other substances have exhibited these properties in our opinion. We mention in particular the definite compound Mn_4N, which was

---

[1] C. Guillaud, thesis, Strasbourg (1943).