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.
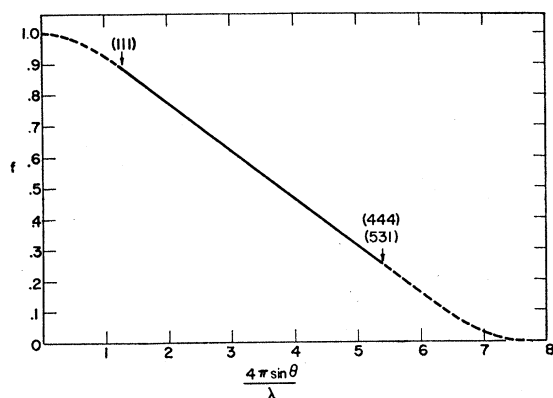

FIG. 8. Magnetic amplitude form factor for $NiFe_2O_4$ obtained from Bragg reflections.

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^{+++}
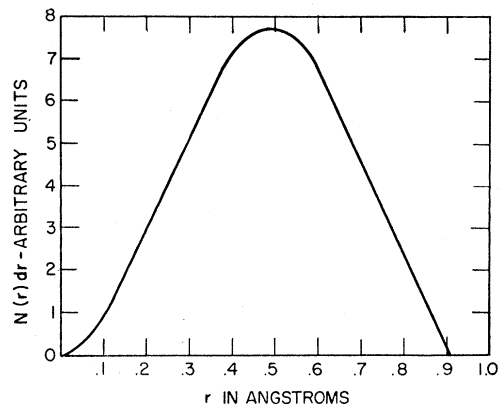

FIG. 9. Radial distribution of "$3d$" electrons in $NiFe_2O_4$ obtained from inversion of form factor in Fig. 8.

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 Néel 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.

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[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

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

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
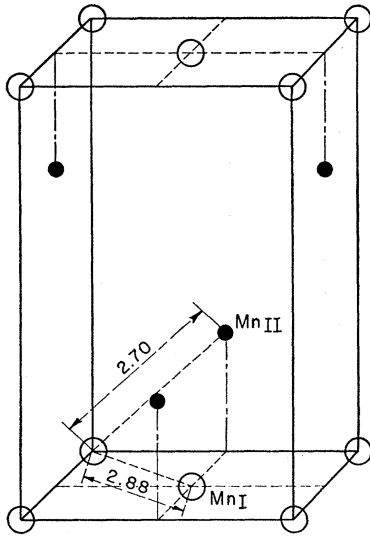
FIG. 1.

studied with Wyart[2] as co-worker, the saturation moment of which can be explained by an analogous mechanism.

In the diagrams of alloys of composition close to Mn_4N, superstructure lines appear with lattice spacings of 3.8A and 2.71A corresponding to the planes (100) and (110), respectively; they are caused only by the diffraction of the nitrogen atoms. In the close-packed cubic lattice which contains 8 tetrahedral holes located at the centers of the cubes and 4 octahedral holes located at the middle of the edges, the nitrogen atoms could be imagined to be distributed at random in the octahedral holes which are the largest. The x-ray diagrams show that the nitrogen atoms are regularly arranged in the centers of the cubes (Fig. 2).

In order to explain the resultant moment, which we find is very close to one Bohr magneton, we have considered two different states of the manganese atoms: $3d^5 4s^2$ for the atom at the corner of the cube and $3d^8$ for the three atoms at the centers of the faces. With an antiparallel arrangement of the spins of the two groups
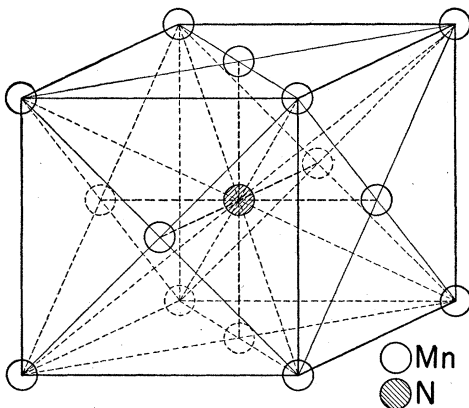

FIG. 2.

○ Mn
◙ N

[2] C. Guillaud and J. Wyart, Recherches du Centre National de la Recherche Scientifique No. 123 (1947).

of manganese atoms we then obtain a resultant moment equal to $3 \times 2 - 5 = 1$ Bohr magneton in agreement with the experimental moment. The distinction between the Mn atoms is supported by the difference in the distances to the nitrogen atom; this should result in the ionization of the manganese atoms which are nearest to the nitrogen atom. We have likewise proved this mechanism by the spontaneous magnetization curve (Fig. 3). The distance of 2.72A which we found between manganese atoms of the two groups therefore would give rise to negative interactions.

We shall compare the properties of Mn_4N with those of Fe_4N,[3] which we prepared and investigated and which also exhibits a superstructure which is identical to that of Mn_4N. The saturation moment of Fe_4N is 2.20 Bohr magnetons, equal to that of iron. In this case, the mechanism of antiferromagnetism probably does not operate. The distances causing negative interactions obviously are different for the manganese atoms and the iron atoms.

We also advanced the hypothesis of negative interactions in solid solutions of manganese arsenides and
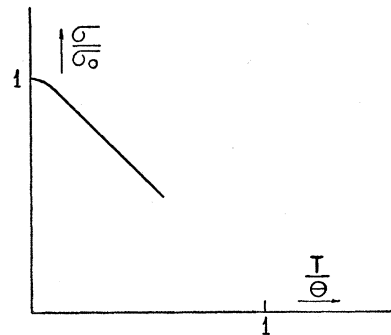

FIG. 3.

antimonides.[1] In the manganese antimonides, the variation of the saturation moments with composition leads us to believe that the Mn atom which enters into solution is in the $3d^5$, $4s^2$ state, the other manganese atoms being in the $3d^7$ state, as we demonstrated. The solid solution limit ends when an Sb atom is replaced by a Mn atom and the experimental saturation moment which is found for this limit is in good agreement with the discussed mechanism of antiferromagnetism.

An additional factor is supplied by this study. The distance 2.78A should also give rise to negative interactions.

We shall probably find this same mechanism in the manganese arsenides,[1] although our investigations in this field are less accurate. The manganese atom which replaces for the arsenic atom should be in the $3d^5$, $4s^2$ state, with an antiparallel arrangement of the manganese atoms in the basic planes.

We supplement these results with results relating to the definite compound Mn_2As. We prepared a single crystal of the Mn_2As compound, which denotes the

[3] C. Guillaud and H. Creveaux, Compt. rend. 222, 1170 (1946)

limit of ferromagnetism of manganese-arsenic alloys. The results obtained until now enable us to consider the Mn atoms as arranged in alternate planes. We advance the hypothesis of a mechanism of antiferromagnetism between two adjacent planes. Thus Mn_2As would have a perfectly compensated antiferromagnetism.

We assume that this mechanism of antiferromagnetism likewise operates in the compound MnP,[4] the consecutive planes being occupied by atoms in the $3d^5$, $4s^2$, and $3d^7$ states. This hypothesis is supported by the small moment which we found experimentally and which is slightly higher than 1 Bohr magneton, We also call attention to the very great variation of the Curie point with field strength for MnP.

This mechanism which we observed in manganese alloys, however, is not peculiar to manganese. We investigated in particular the compound $CrTe$[5] and the small moment which is found, 2.40 Bohr magnetons, seems to be explicable by a mechanism of antiferromagnetism.

We shall supplement these data on the distances causing negative interactions in manganese alloys by data on the lower limit of positive interactions which result in ferromagnetism. If the Curie points of the definite compounds, MnBi, MnSb, and MnAs are

[4] C. Guillaud and H. Creveaux, Compt. rend. **224**, 266 (1947).
[5] C. Guillaud and S. Barbezat, Compt. rend. **222**, 1224 (1946).

plotted against the effective distances between manganese atoms, the lower limit of the distances giving rise to positive interactions is found to be about 2.81A.

R. SMOLUCHOWSKI, *Carnegie Institute of Technology, Pittsburgh, Pennsylvania:* From your experimentally determined form factor you calculated the radial density distribution of the $3d$ electrons. How does this distribution compare with the results of theoretical calculations based either on the Fermi or the Hartree method? Would this indicate the location of the unpaired spins in the $3d$ shell?

J. C. SLATER, *Massachusetts Institute of Technology, Cambridge, Massachusetts:* In answer to this question I may say that the radius of the $3d$ shell as obtained from these neutron diffraction data is smaller than the theoretical radius. We really do not understand why it is so and what this signifies.

L. M. CORLISS, *Brookhaven National Laboratory, Upton, Lond Islang, New York:* One should add also that the results are average values for the $3d$ shells of nickel and of iron atoms in the nickel ferrite. Also the atoms do not occupy equivalent sites in the lattice so that a direct interpretation of our radial density distribution is not simple.