

Intradomain Magnetic Saturation and Magnetic Structure of γ -Fe₂O₃

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The average moment for γ -Fe₂O₃ was found to be 1.18 Bohr magnetons per iron atom, which supports a preferential distribution of iron vacancies on octahedral sites in a spinel structure. A sample motion ballistic method was used for direct measurement of magnetic moments.

THE saturation magnetization of gamma iron (III) oxide¹ has been investigated in the liquid helium range to test speculation² regarding the magnetic structure as determined by the positions and orientation of Fe⁺⁺⁺ in γ -Fe₂O₃. The network of iron atoms is a partially depleted magnetite (inverse spinel) structure as can be demonstrated by similarity of x-ray patterns for magnetite and γ -Fe₂O₃; therefore, one may assess the magnetic structure from a determination of the net saturation magnetization of a sample at 0°K. In the inverse spinel structure,³ each Fe⁺⁺⁺ is either at the center of a tetrahedron with oxygen atoms at the corners, or at the center of an octahedron with oxygen atoms at the corners. The available data⁴ indicate that the magnetic moment of an Fe⁺⁺⁺ in a tetrahedral site cancels the moment of an Fe⁺⁺⁺ in an octahedral site. The net moment density is dependent on the excess of octahedral Fe⁺⁺⁺ over tetrahedral Fe⁺⁺⁺; that is,

$$\sigma_s^0 = \mu_0 N_c (x_0 n_0 - x_t n_t), \quad (1)$$

where μ_0 is the atomic moment (5 Bohr magnetons for Fe⁺⁺⁺), N_c is the number of cells per cubic centimeter, n_0 and n_t are numbers of available octahedral and tetrahedral sites, respectively, per unit cell, and x_0 and x_t are the degrees of occupation of the respective sites. The magnetization (average) for γ -Fe₂O₃ in Bohr magnetons per atom is given by

$$\bar{\mu} = \frac{3\sigma_s^0}{8N_c n_t} = \frac{3\mu_0(2x_0 - x_t)}{8}. \quad (2)$$

Thus, the problem is to determine the combination of x_0 and x_t which will yield the experimental value of $\bar{\mu}$ which we determine. We consider two cases: (1) random distribution, in which x_0 and x_t are equal and (2) the case in which the tetrahedral sites are filled ($x_t = 1$) and all the vacancies are at octahedral sites. The experimental moment is used to distinguish the two cases.

The experimental procedure used here for measuring

magnetic moments has been previously used for magnetic saturation studies.⁵ Briefly, it consists of two measuring coils wound in series opposition and also in series with a ballistic galvanometer. The sample is moved from the center of one coil to the center of the other in a short time compared with the period of the galvanometer, whereupon the deflection of the galvanometer is proportional to the magnetic moment of the sample. The results obtained for γ -Fe₂O₃ are shown in Fig. 1. The absolute value of the magnetic moment is determined by comparing with results for metallic iron at 4.2°K (using the same equipment) and taking the iron moment as 2.22 Bohr magnetons per atom. The magnetization as a function of field at 4.2°K is shown in Fig. 1. Since the magnetization does not change within the experimental error from 4.2°K to 1.3°K, it is assumed that this value is the value at 0°K. This average value is 1.18 Bohr magnetons per atom of iron, if one assumes pure Fe₂O₃. Chemical analysis shows the presence of 3% impurities of which only 0.03% (MnO) contributes to the magnetization. A concentration of 1.7% of divalent iron was found. If one assumes a random distribution of vacant sites in the spinel structure over the two types of sites

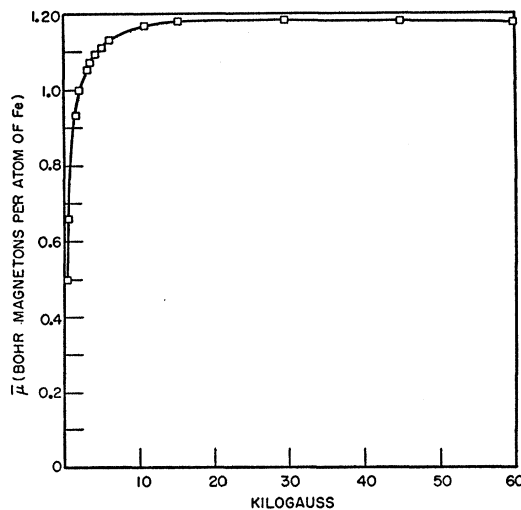


FIG. 1. Plot of average magnetic moment ($\bar{\mu}$) of γ -Fe₂O₃ as a function of magnetic field (H). The temperature is fixed at 4.2°K in liquid helium.

¹ Procured through the courtesy of Minnesota Mining and Manufacturing Company.

² W. P. Osmound, Proc. Phys. Soc. (London) **65**, 121 (1952); L. Néel, Ann. phys. (12) **3**, 137 (1948); E. J. Verwey and E. L. Heilmann, J. Chem. Phys. **15**, 174 (1947); E. J. Verwey, Z. Krist. **91**, 65 (1935).

³ A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1945), p. 334.

⁴ E. W. Gorter, thesis, University of Leiden, 1954 (unpublished), p. 46.

⁵ W. E. Henry, Phys. Rev. **88**, 559 (1952); **94**, 1146 (1954).

($x_0 = x_i$), the average moment would be 1.66 Bohr magnetons per atom of iron. On the other hand, if it is assumed, as was predicted² by Néel and by Verwey (on the basis of x-ray studies) that there is a selective iron vacancy formation limited to octahedral sites ($x_i = 1$) the average moment is 1.25 Bohr magnetons per atom of iron for pure Fe_2O_3 . For a sample of the described composition, the average moment would be 1.19 Bohr magnetons per atom of iron. Our results of 1.18 ± 0.02 Bohr magnetons per atom of iron is in good agreement with this theoretical value for a restricted distribution. That is, in view of the 1.66 Bohr magnetons per atom required for a random distribution

and 1.19 required for deficiencies restricted to octahedral sites, it can be said that the magnetization experiment supports the preferential distribution. An alternative possibility, based on hydrogen atoms in the lattice on octahedral sites, has been suggested by Braun.⁶ The resulting moment (one Bohr magneton per atom of iron) would, however, not be in keeping with the moment obtained in the present investigation. Further study is being made of magnetic properties of oxygenated compounds of iron. Our appreciation is extended to Mr. Dean Walter of the Naval Research Laboratory for analysis of the samples.

⁶ P. B. Braun, *Nature* **170**, 1123 (1952).

Significance of Hall Effect Measurements on Alloys*

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Hall effect data for a number of alloys are examined in the light of the accepted theory of this effect. It is concluded that assumptions made about the relaxation time which seem appropriate when scattering by lattice vibrations predominates are not valid when scattering by solute atoms becomes significant.

IN recent years a number of investigations of the variation of the Hall constant (R) as a function of composition in alloys have been carried out. In particular, a series of papers by Pugh and his co-workers¹⁻³ has shown that important indications of the electronic structures of ferromagnetic transition metal alloys can be obtained from such measurements.

It is well known that the Hall constant is related to n , the number of electrons per atom, by the expression

$$R = 1/(Nnec),$$

where e is the electronic charge, c the velocity of light, and N the number of atoms per unit volume, only for metals in which the Fermi surface takes certain simple forms. Even in the noble metals, which have one conduction electron per atom and a half-full Brillouin zone, the value of n^* [defined as $1/(RNec)$] is not exactly 1.0. Recent measurements of the thermoelectric powers of silver alloys⁴ in which the number of conduction electrons has been reduced to slightly less than 1.0 per atom suggest strongly that the anomalously positive sign of the thermoelectric power of pure silver is due to the presence of electrons in states near some Brillouin zone boundary where the energy departs from the free-

electron value. The occupation of such states by the electrons of highest energy is probably also responsible for the departure of n^* from unity. The present note is intended to draw attention to evidence that in alloys R departs from the free-electron value to an extent that cannot reasonably be explained in terms of distortions of the Fermi surface. There are strong grounds for believing that when both lattice scattering and impurity scattering are present, discussions of Hall effect data must take the scattering mechanisms into account.

Hall effect data are available for the silver-gold alloys over a wide range of compositions and temperatures,⁵ and n^* values derived from them are shown in Fig. 1. The room temperature values for the alloys are greater than those of the pure metals, but it is conceivable that these increases are due to increases in the Fermi surface distortions present in the pure metals. At low temperatures, however, n^* becomes still greater for the alloys, while approaching unity for the pure metals. This peculiar temperature variation and the very large low-temperature values show clearly that in the alloys there exists some factor, not present in the pure metals, which plays an important part in determining the value of R .

By adding 40 atomic percent of palladium to silver, the number of conduction electrons can be reduced to 0.6 per atom without d -band holes being created. These electrons might be expected to be described extremely

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¹ A. I. Schindler and E. M. Pugh, *Phys. Rev.* **89**, 295 (1953).

² S. Foner and E. M. Pugh, *Phys. Rev.* **91**, 20 (1953).

³ E. M. Pugh, *Phys. Rev.* **97**, 647 (1955).

⁴ J. C. Taylor and B. R. Coles, *Phys. Rev.* **99**, 614 (1955). (Further details of this work will be published shortly.)

⁵ K. Onnes and B. Beckman, *Proc. Acad. Sci. Amsterdam* **15**, 307, 319, 664 (1912).