Magnetization Studies and Possible Magnetic Structure of Barium Ferrate III

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An approach to the absolute saturation magnetization of polycrystalline, magnetically hard $BaO \cdot 6Fe_2O_3$ has been achieved by using magnetic fields up to 60 000 gauss and temperatures down to 1.3°K where the saturation magnetization and remanence (about one-half of the saturation magnetization) have become temperature-independent. The magnetization in the highest fields is approaching 1.64 Bohr magnetons per atom of Fe at 1.3°K and 1.13 at 295°K. Inferences are drawn as to a possible magnetic structure from such a saturation magnetization. A sample displacement ballistic technique is used.

INTRODUCTION

THE discovery[1] of magnetically hard barium ferrate III ($BaO \cdot 6Fe_2O_3$) caused considerable speculation as to its magnetic nature, although the marked temperature dependence of the remanence made it unsuitable for practical applications. Attempts to reach saturation magnetization of the polycrystalline specimens failed because of field and temperature limitations. There was, however, an easy direction of magnetization in single crystals which permitted measurement of a directional saturation magnetization in this direction.[2] This saturation magnetization was found to increase linearly as the temperature decreased and an extrapolation was made in temperature to estimate the absolute saturation magnetization.

Several questions arise in connection with the saturation magnetization of paramagnetic and ferromagnetic substances and the theories which attempt to explain them. That is, while some ferromagnetic substances, such as gadolinium metal[3] and Cr^{+++} in anhydrous chromium chloride[4] yield the full, expected saturation magnetization, most ferromagnetic substances yield absolute saturation values lower than would be expected from the simple, assumed structures of individual ions or atoms. Examples are: Iron[5] (2.2 instead of 4 Bohr magnetons per atom of iron), neodymium[6] (1.6 instead of 3.3 Bohr magnetons per atom), ferrites,[7] uranium hydride,[8] and others.

There are essentially three theories purporting to account for this reduction of expected saturation magnetization, viz., (1) the Néel sublattice theory[9] of ferrimagnetism, based on partial cancellation of moments due to oppositely oriented sublattices and supported for some substances by neutron diffraction work[10] and some saturation data[7]; (2) the Gal'perin-Vonsovskii theory[11] in which the interatomic distances, the interaction between the free s electrons and the d electrons play roles in cancellation of the magnetization normally expected to arise from d electrons. The effect of distance between neighbors is borne out by the pressure dependence of saturation magnetization; and (3) the Weiss and DeMarco theory[12] based on the promotion of d electrons to higher nonmagnetic states.

The purpose of this investigation was to obtain absolute saturation magnetization of this magnetically hard barium ferrate III by application of high fields at low temperatures and further to determine if the saturation magnetization and remanence become temperature independent at sufficiently low temperatures; in addition to obtaining a better understanding of magnetic interactions, one may infer the magnetic structure of $BaO \cdot 6Fe_2O_3$ by comparison of its absolute saturation magnetization with that of gamma iron oxide[13] and with the values expected in various theories.[9,11]

EXPERIMENTAL METHOD

The experimental method has been previously described[14] in which a sample is moved from the center of one coil to the center of another coil, the two collinear coils being wound in series opposition with each other and in series with a ballistic galvanometer, the deflection being proportional to the magnetic moment of the sample. The calibration was carried out with pure iron using 2.22 Bohr magnetons per atom as the absolute saturation magnetization for iron. The compact sample of $BaO \cdot 6F_2O_3$ weighed 25 grams and was in the form of a cylinder 2.5 cm in diameter and 1.4 cm long. A

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metal Dewar for liquid helium was used[15] and magnetic fields up to 60 000 gauss were obtained by a magnet of the Bitter type.[16] The sample was obtained from Crucible Steel Company through the courtesy of Lieutenant Kenneth Cole. Analysis of the sample by Mr. Dean Walter of the Naval Research Laboratory showed it to be stoichiometric to within a fraction of a percent.

RESULTS AND DISCUSSION

Figure 1 shows a plot of magnetization as a function of magnetic field for four temperatures. It is seen that for room temperature (295°K) the zero field magnetization is 0.55 Bohr magneton per atom of iron and with application of magnetic field, rises slowly until at 30 000 gauss, the domain alignment is practically complete; the application of an additional 30 000 gauss is a small addition with respect to the molecular exchange field and also small with respect to kT/μ (the thermal energy divided by the moment). Thus, very little increase takes place in the magnetization which must arise from intradomain magnetization. At 130°K, the zero field magnetization (remanence) is 0.78 Bohr magnetons per atom of iron and saturates at a little less than 1.60 Bohr magnetons per atom of iron. From 130°K down, the magnetization in a given field is not very much dependent on temperature and in the range 4.2–1.3°K the difference in constant field magnetization for different temperatures in this range is not detectable. At 4.2°K the zero field magnetization is 0.80 Bohr magneton per atom of iron and rises to an absolute saturation magnetization value of 1.62 Bohr magnetons per atom at 60 000 gauss. This extrapolates, field wise, to a value of 1.64 Bohr magnetons per atom for the absolute saturation magnetization, a value applicable to the polycrystalline material and hence applicable to all directions. The absolute saturation magnetization here measured can be analyzed in terms of either the Néel theory or the Gal'perin-Vonsovskii theory.

In terms of the Néel theory based on opposite orientation of magnetic ions occupying A and B sites, one can think of the hexagonal close packed structure[17] of barium ferrate III as nearly the same as a spinel structure since a large portion of the unit cell has this structure in fact. For gamma Fe₂O₃, whose saturation magnetization is 1.2 Bohr magnetons per atom of iron, a Néel structure was found compatible with the results, provided one assumes that the vacant ion sites are preferentially distributed on octahedral sites with the moments on octahedral sites cancelling those on tetrahedral sites. That is, the difference is $\frac{1}{4}$ of the total occupied sites. Using this model, with a random
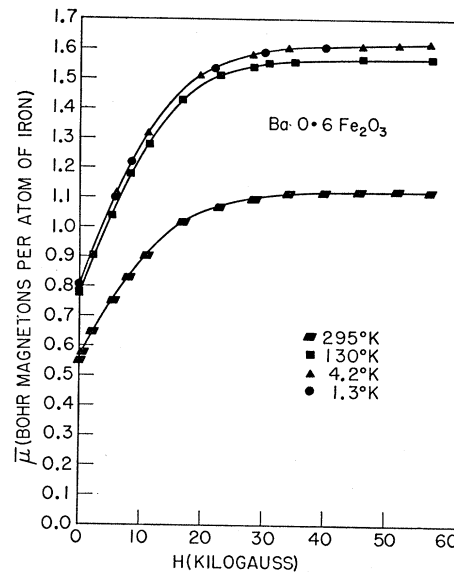
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FIG. 1. Plot of magnetization (μ) as a function of magnetic field (H) for barium ferrate III at four temperatures.

distribution of Fe⁺⁺⁺ among the available B type and A type sites, a moment of 1.67 Bohr magnetons per atom results. This compares favorably with the experimental value.

On the other hand, the Gal'perin-Vonsovskii model is compatible with the experimental results, for this model, based on interatomic distances, number of nearest neighbors, and a constant calculable in principle from quantum mechanics, yields a moment of 1.60 Bohr magnetons per atom of iron from the formula

$$m = N_d - (2b-1) \mp k_1(d_1-D) \mp k_2(d_2-D), \quad (1)$$

where N_d is either the number of electrons or holes (whichever is smaller) in the d shell; k is calculated from the number of nearest neighbors, that is, k_1 equals $7.7Z_1/12$, and k_2 is $7.7Z_2/12$, where Z_1 is the number of nearest neighbors (magnetic) and Z_2 is the number of next to nearest neighbors; d_1 is the distance to nearest neighbors and d_2 is the distance to next nearest neighbors; D is the sum of the radii of the d and s shells and b is the degree of spinel inversion.

This study has shown that at low temperatures both the saturation magnetization and remanence become temperature independent at low temperatures. It has produced absolute saturation in polycrystalline, magnetically hard BaO·6Fe₂O₃ and has yielded a value 1.64 Bohr magnetons per atom of iron for the absolute saturation magnetization. This saturation magnetization calls for a random distribution of vacancies with respect to iron ions on the Néel model while at the same time the saturation magnetization at absolute zero found experimentally does not disagree with the detailed model of Gal'perin and Vonsovskii.