mal variation in the dielectric constant of glasses at very low temperatures. From our observations we have derived electric dipole moments associated with transitions within two-level systems in glasses. If one thinks of these two-level systems in terms of moving groups of atoms, our experiments show that the corresponding electrical charge is higher in borosilicate glass than in vitreous silica.

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Spontaneous Magnetization Reversals in Magnetite in the Verwey Transition Region

R. A. Buckwald, A. A. Hirsch, D. Cabib, and E. Callen*†

Physics Department, Technion - Israel Institute of Technology, Haifa, Israel

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A magnetite rod has been observed to rotate suddenly at up to six discrete temperatures between 110 and 183 K in a weak magnetic field (1.5 Oe).

We have observed three, four, and sometimes six reversals in the direction of magnetization of samples of polycrystalline synthetic magnetite as well as of natural single crystals of the oxide as the temperature is raised through the Verwey temperature ($T_V \simeq 119$ K). We magnetize the sample along its long axis in a large field (about 10 kOe), cool it to liquid air temperature (while holding it in a keeping field of 50 Oe to maintain the remanent magnetization), and then lower the field (H) to 1.5 Oe. The sample is placed within a cryostat and gradually warmed, over a period of up to 8 h at a rate of 0.25 ± 0.05 K per minute. In the 1.5-Oe field, the sample rotates many times, coming to rest after swinging through any integral multiple of 180°. In general, the appearance of the discrete jumps of 180° varied from trial to trial. In some samples the jumps are accompanied by smaller rotations due to intermediate nonaligned orientations. Figure 1 exhibits typical angle-versus-temperature curves for four different samples. Figure 2 shows an example of the frequency of occurence of the large discrete rotations of a sample of synthetic magnetite.

We think this is a unique phenomenon; so far as we know, there is no other material with more than one magnetization reversal. Magnetization reversal in magnetite is well known in the rock magnetization literature.[1] A single self-reversal in the direction of the remanent magnetization of a single crystal at 130 K was first reported by Yama-ai, Ozima, and Nagata.[2] These investigators found that the self-reversal was critically dependent on the shape of the sample; that is, the shorter the sample, the more pronounced was the self-reversal. In order to explain this reversal they assumed that there are two different kinds of magnetic domains which are coupled with each other by magnetostatic forces.

In our samples, which have a rod shape, we observe a large number of discrete 180° rotations only when they are many times as long as they are thick. We believe that our rods in their initial remanent states behave as single domains. The low frequency of observations of 180° rotations at higher temperatures (Fig. 2) may be due to the introduction of multiple domains in the samples after several successive reversals. Do-

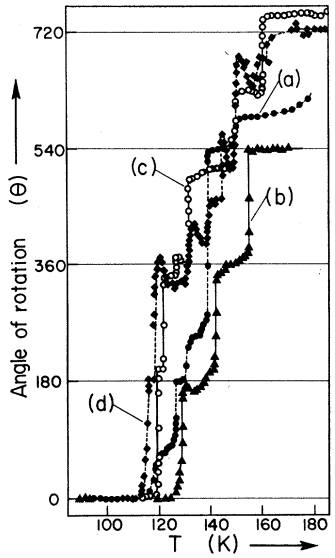

FIG. 1. Typical angle-versus-temperature curves showing the jumps in rotations of magnetite rods: *a*, sample prepared in CO_2 and quenched in liquid nitrogen; *b*, sample prepared in CO_2 and cooled slowly to room temperature; *c*, sample prepared in CO_2/CO and quenched in argon atmosphere; and *d*, natural single crystal of magnetite.

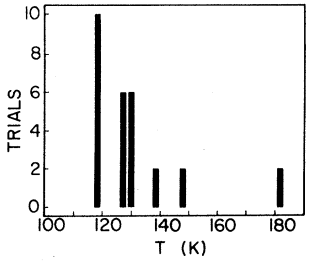

FIG. 2. Frequency of occurence of rotations at different temperatures of a sample of synthetic magnetite.

main effects may play some role in the intermediate nonaligned orientations of the rod (Fig. 1).

The apparatus provides the samples with a nearly torque-free suspension by a 2-m-long, enclosed, 0.1-mm-diam nylon thread. The temperature is controlled by a commercial control unit which cools by controlling the flow of liquid nitrogen through two copper cooling coils placed above and below the sample. The temperature is found to vary less than ± 0.05 K across the sample. The sample is provided with a bias field by means of two Helmholtz coils such that when aligned with the earth's magnetic field, a uniform horizontal field is obtained across the sample to better than ± 1%. The cryostat is provided with a window and the sample is attached to a plastic indicator such that sample angle is read externally to ± 0.5°.

A number of kinds of samples were examined to ensure that the observed effect was not due to some sample irregularity or nonuniformity. Synthetic rods were prepared from 2 to 5 cm in length, keeping a length-to-diameter ratio of greater than 15.

The rods were prepared on the basis of the Darken and Gurry phase diagram.[3] In general, samples were prepared by placing pure iron in a furnace in a CO_2 environment at 1390°C for up to 24 h. They were then quenched in liquid nitrogen (quenching time of about 3 sec). To ensure that they were stoichiometric (i.e., that partial pressure of O_2 is less than 10^{-4} atm), a set of them was prepared in a cleaned and dried atmosphere of $CO_2/CO = 250/1$ giving a measured partial pressure of oxygen $P_{O_2} = 10^{-5}$ atm. Quenching was done through an argon atmosphere. Some samples were cooled slowly to room temperature to see if quenching affected the results. In addition, the rough outer 0.5 mm of surface was removed from some samples to see if the macroscopic surface irregularities affected the results.

The following tests were made on stoichiometry and structure: Samples were found to be stoichiometric by weight to within 1 part per 1000; structure was confirmed by comparison with the latest U. S. National Bureau of Standards powder x-ray data; resistivity was tested near the Verwey point and found to agree with the existing stoichiometric data; Mössbauer spectra were taken and checked for signs of hematite (none were found); furthermore, Mössbauer spectra exhibited the characteristic spectral changes recorded in literature. Also, a natural single crystal was placed in the cryostat in order to see if some property of polycrystalline structure produces the magnetization reversals.

In all, 25 samples were examined. In every case, the results were found to exhibit essentially the same rotation characteristics at slightly different temperatures in the range 110–183 K.

It seems to us that the net magnetic moment of the low-temperature insulating phase of magnetite reverses as the temperature reaches several critical values even when no magnetic fields are applied. The rotation of the rod is, of course, due to spin-orbit coupling. Without it, the full

spin system would simply flop over at the transitions, so as to maintain the net moment along the field. Because of the coupling to the lattice, when the spin system rotates it drags the rod around with it. This rotation process is sensitive to the field strength. If the field is too large, before the rod has a chance to rotate, the moment flops over by itself.

In 1932, Li[4] discovered a discontinuity in the technical magnetization (ΔM) near the Verwey temperature, T_V, the temperature at which Fe^{3+} and Fe^{2+} ions order on the B sites. The sudden drop in magnetization as the temperature is reduced was later confirmed by Domenicali.[5] It is usually believed that ΔM results from the large magnetocrystalline anisotropy below T_V.[6] Since the electron ordering is usually considered to involve only valence electrons on B sites, all of whose spins are presumed to be parallel, and since the Verwey temperature (119 K) is much below the Néel temperature (855 K), so that the sublattice magnetizations are expected to be substantially saturated (i.e., simple spin-wave theory should apply), it might be expected that there would be little change in the gross magnetic properties at the Verwey transition. It was indeed suggested[7] that the lowest branch of the spin-wave spectrum would be unaffected by the ordering (not necessarily the upper branches), and Alperin *et al.*,[8] studying inelastic neutron scattering, confirmed this.

Recently there began a number of startling developments which have altered our picture of magnetite. Yamada, Suzuki, and Chikazumi,[9] by electron diffraction, showed the ordered structure to be far more complex than Verwey had envisioned. Interpretation of the diffraction patterns requires some sort of ordering along the two basal plane axes of the orthorhombic unit cell of the ordered phase, as well as along the c axis, and the unit cell must be doubled along the c axis. Neutron diffraction studies of the ordered phase[10] gave the same result, and Mössbauer spectra,[11] resolved into five individual components, suggested five different crystalline sites. At the same time, Cullen and Callen and others[12] gave a three-order-parameter band treatment. This model provides an explanation for the diffraction patterns (the authors did not include an order parameter corresponding to doubling of the unit cell along the c axis), the numerous hyperfine fields, Mössbauer[11] and NMR[13] spectra, and the peculiar temperature dependence of the conductivity.[14]

The experimental evidence is pointing toward a series of transitions. Westrum and co-workers[15] discovered two peaks in the heat capacity of pure synthetic ceramic magnetite, at 113.3 and at 118.8 K. They also interpreted changes in the shape and intensities of Mössbauer lines,[16] at about the same temperatures, to arise from two separate transitions. Wolf and Cornell[17] confirm the two specific-heat peaks and see suggestive evidence of a third, small, unresolved peak between them. Buckwald and Hirsch[18] interpret their own Mössbauer spectra to suggest not only the two transitions discovered by Westrum and Evans, but also at least three more transitions at higher temperatures. It is possible for a multiple-order-parameter theory to account for a whole series of transitions. In fact, Ihle and Lorentz[19] and Tanaka and Chen[19] show that the metal-insulator transition can occur at a different temperature from the charge order transition even when only one order parameter (Verwey order, along the c axis) is assumed. But how is one to account for a half-dozen magnetization reversals?

A complex spin structure is neither confirmed nor ruled out by the existing neutron-diffraction evidence. Alperin *et al.*,[8] to magnetize the sample, employed a field of about 10 kOe. Since 1380 Oe is sufficient to eliminate the kink in the magnetization[5] at 110 K, it could be argued that the field has supressed the formation of spirals. Samuelson *et al.*,[10] like Alperin, employed the polarized-beam method, and therefore also used a magnetizing field. Fujii, Shirane, and Yamada[20] have recently reported neutron-diffraction studies, performed with no field on. Lines are observed which are forbidden in the cubic structure. The lines have a strong temperature dependence in the range 119–130 K. Fujii, Shirane, and Yamada consider the lines to be of phonon origin, but it could be that some of the scattering is coming from an angled spin structure.

Perhaps the strongest evidence militating against spiral spins is from NMR. Rubinstein[21] observes a set of absorptions at 8 kOe the same as at zero field. All lines shift rigidly together, rather than collapsing to a reduced set of lines, as one would expect if a spin spiral collapsed in a field.

Recently, Hirsch, Kronmüller, and Walz[22] discussed the low-field magnetic after-effect of the insulating phase of magnetite, assuming a five-parameter electronic transition among the ions (coupled by AA, AB, and BB exchange interactions) between five kinds of pairs.[23] The changes

in the charge density of the individual iron ions may be accompanied by changes in the spin density. As shown by Buckwald and Hirsch,[18] the line intensity rearrangements of Mössbauer spectra in magnetite have a strong temperature dependence and suggest a multistage electronic transition in the Verwey-temperature range. At least five different spin densities may be responsible for the resolved Mössbauer spectral components.

The fact that the discrete magnetization reversals occur in the same temperature range in which the discrete stages in the line-intensity rearrangements in the Mössbauer patterns are observed suggests that spin-density changes may be involved in the observed magnetization reversal phenomenon. The insulating phase of magnetite in which several electronic transitions may take place seems to be more stable when no magnetic fields are applied. Recently, Kamilov, Musaev, and Shakhshaev[24] have observed that the two heat-capacity discontinuities are more intense and more separated in a zero field then in a field of 3.4 kOe.

We are just now investigating the effect of a magnetic field on the specific heat and on the electric conductivity.

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*Visiting Professor, on sabbatical leave from American University, Washington, D. C. 20016, Fall, 1974.

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