

Weak Ferromagnetism in Antiferromagnetic UO_2 †

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(Received 5 December 1966)

A nearly isotropic weak ferromagnetism has been observed by the torque method in single crystals of UO_2 below the Néel temperature. Measurements were made of remanence produced by cooling samples from $T > T_N$ down to 4.2°K in fields up to 32 kOe or by cooling in zero field to 4.2°K followed by the isothermal application of the field. The largest remanence observed was 5.7×10^{-2} emu/g. Upon warming from 4.2°K toward T_N , the remanence diminishes with increasing rapidity and then levels off abruptly at T_N at a small residual value. The curve of remanence versus temperature is markedly different for the two types of magnetic treatment.

WE have observed a nearly isotropic weak ferromagnetism in single crystals¹ of uranium dioxide below the antiferromagnetic ordering temperature of about 31°K. A small remanent magnetization can be induced either by cooling the sample through the Néel temperature (T_N) in a magnetic field ("field-cooling") or by first cooling in zero field to low temperature and then applying a magnetic field ("isothermal treatment"). The largest remanence observed was 5.7×10^{-2} emu/g, produced by cooling a sample in a field of 32 kOe. This amounts to $2.8 \times 10^{-3} \mu_B$ per uranium ion. This effect is similar to the weak ferromagnetism observed in the cubic antiferromagnets UMn_2 ² and $\alpha\text{-Mn}$.³

In all field-cooling experiments the cooling field was turned on with the temperature greater than T_N and remained on while the sample was cooled to 4.2°K. In the isothermal-treatment experiments the sample was cooled to 4.2°K and then subjected to the treatment field for a short time. The magnitude and direction of the remanent magnetization was then determined by measuring the torque exerted by a small uniform magnetic field which could be rotated in the plane perpendicular to the axis of suspension. The measuring field was kept small enough not to disturb the remanent magnetization; the maximum field that could be used depended on the strength of the remanence being measured. Remanence produced by fields of 15 kOe or less was measured with a field of 0.5 kOe or 1 kOe, while remanence produced by fields greater than 15 kOe was measured with a field of 2.5 kOe.

Figure 1 shows the dependence of the remanence of the cooling or treating field. As an example of the magnitude of this effect we note that cooling of samples 3 and 4 in a field of 10 kOe produced a remanent magnetization of about 4×10^{-2} emu/g. This magnetization is about $\frac{1}{4}$ the magnitude of that calculated from the equation

$$M = \chi H$$

† Supported by the National Science Foundation and the Advanced Research Projects Agency of the Department of Defense.

¹ Samples were kindly lent to us by Dr. B. T. M. Willis, Atomic Energy Research Establishment, Harwell, England.

² S. T. Lin and A. R. Kaufmann, *Phys. Rev.* **108**, 1171 (1957).

³ H. W. Cooper, A. S. Arrott, and H. W. Paxton, *J. Appl. Phys.* **32**, 2506 (1961).

for a field of 10 kOe, using the published⁴ value for χ of 1.6×10^{-5} in cgs units.

The remanent magnetization vector lay almost parallel to the direction of the cooling or treating field and its magnitude was essentially independent of the direction of that field. In measurements with a cooling field of 12 kOe applied in various directions in the (100)

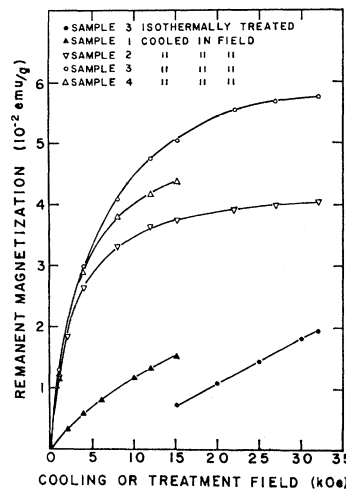


FIG. 1. Remanent magnetization measured at 4.2°K versus cooling or treatment field applied along [100].

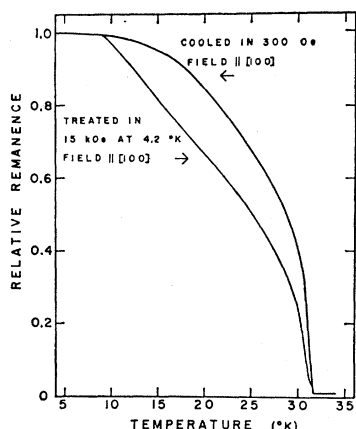
plane we found that the direction of the remanence never deviated by more than 2° from the cooling-field direction. The magnitude varied by less than 5%. Measurements in the (110) plane also showed a low degree of anisotropy.

Figure 2 shows the decay of the remanence as the sample warms up from 4.2°K to the Néel temperature. The striking feature of these curves is the sudden change in slope at T_N , which clearly indicates that the weak ferromagnetism involves the ordered magnetic structure. Our value of 31.5°K for T_N agrees to within the absolute accuracy of our temperature measurements with that of Willis and Taylor, who found $T_N = 30.6$ °K.⁵ If the sample is allowed to warm up from 4.2°K to a temperature less than T_N and is then cooled again,

⁴ M. J. M. Leask, L. E. J. Roberts, A. J. Walter, and W. P. Wolf, *J. Chem. Soc.* **1963**, 4788 (1963).

⁵ B. T. M. Willis and R. J. Taylor, *Phys. Letters* **17**, 188 (1965).

FIG. 2. Remanent magnetization versus temperature as sample warms up from 4.2°K.



there is a partial recovery of the remanent magnetization. The small remanence left after the transition varied from sample to sample; it was never more than 10% of the remanence at 4.2°K and was gone by the time the sample reached room temperature.

There is a noticeable difference in shape between the curves for the field-cooled and the isothermally-treated samples, but in each case we found that the shape of the curve was essentially independent of the amount of remanence produced. The cooling and treatment fields used for Fig. 2 were chosen to give roughly the same remanent magnetization at 4.2°K. It appears that the difference in temperature dependence is due to a fundamental difference in the two processes.

In addition to these measurements, in which a remanent moment was first produced and then measured with a field sufficiently small to have little effect on it, we have also made measurements of the torque exerted on samples cooled in zero field to 4.2°K by a large field rotated in the plane perpendicular to the axis of suspension. In all samples we observed a typical "rotational hysteresis" torque. Superimposed on this torque, in samples 2, 3, and 4, was an oscillating component having the symmetry of the axis of suspension. Figure 3 shows typical data for both directions of rotation with the sample suspended along the [001] axis. An interesting feature is the displacement in phase of the 4-fold-symmetric torque for the two directions. If the rotation of the field was stopped at some point,

FIG. 3. Torque versus magnetic-field direction for a sample cooled in zero field.

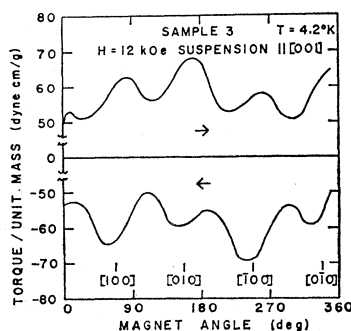
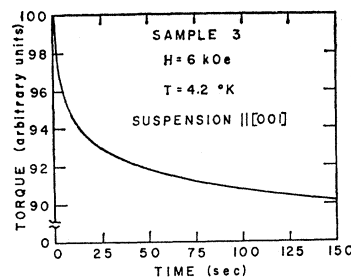


FIG. 4. Torque versus time after rotation of magnetic field is stopped abruptly at $t=0$; sample cooled in zero field.



the torque showed a decay of as much as 12% in time, as shown in Fig. 4. This decay seemed to be independent of the direction of the field when rotation was stopped. At moderate rotation speeds, the torque showed little dependence on rate of rotation.

It appears that the 4-fold torque as well as the dc hysteresis torque is due to a remanent magnetization, produced by the relatively large measuring field, that lags behind the field direction by 30° to 45°, the angle of lag depending on field strength and direction. In order to measure this remanence we stopped the rotation at the desired angle and waited about 1 min before shutting off the field. We then used a field of 0.5 kOe to measure the magnitude and direction of the remanence. Since most of the decay occurs within 1 min after rotation ceases, this procedure eliminated errors due to variation in the time required to reduce the field to zero.

For the case shown in Fig. 3, we found an average lag of 31.6°. In Fig. 5 we plot both the deviation of the remanence from the average 31.6° lag and its magnitude versus the direction of the remanent moment in the (001) plane. The data for both directions of rotation are reasonably consistent. We see that, regardless of the direction of rotation, the remanent moment lags the field by the average angle when the moment lies near the axes of symmetry and tends to deviate from this average lag in the direction of the nearest <110> axis. The remanence is largest when it is along <110> axes and smallest along <100>. The torque plotted in

FIG. 5. Magnitude of remanent moment and deviation from 31.6° lag as a function of the direction of the moment for the case of Fig. 3.

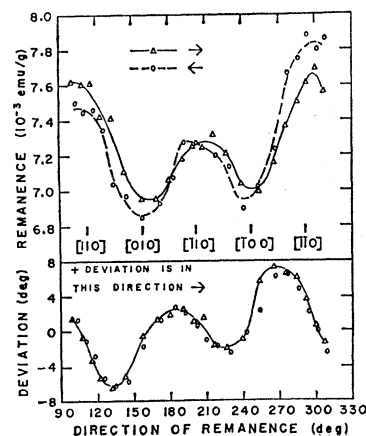


Fig. 3 is reasonably well accounted for by the interaction of this lagging remanence with the 12-kOe rotating field, provided that the effect of the time decay is considered.

The large variation in the magnitude of the weak ferromagnetism from sample to sample and the lack of anisotropy have not been explained. The temperature dependence shown in Fig. 2, particularly the sudden discontinuity in slope at T_N , shows that the remanent moment is connected with the ordering of the spins and is not due simply to the magnetization of a ferromagnetic impurity. UO_2 usually contains an excess of oxygen atoms; however, reduction of sample 1 in hydrogen at 1-atm pressure and a temperature of 600°C for 17 h caused an increase of about 12% in the magnitude of remanence produced by cooling in a field of 15 kOe, and it appears that moderate heating of samples

in air causes a slight decrease in the field-cooling effect. This tends to rule out the possibility of ferrimagnetism due to oxygen-caused defects.

In addition to the measurements on the Harwell crystals, a few measurements were made on two single crystals from the Battelle-Northwest laboratories.⁶ The behavior was qualitatively the same as that of the Harwell samples, although the remanent moments were about $\frac{1}{10}$ those of samples 2-4, and the 4-fold torque was not observed.

While measuring the susceptibility of polycrystalline samples of UO_2 , Arrott and Goldman observed small hysteresis effects at liquid-helium temperature.⁷ This may have been due to the phenomenon reported here.

⁶ We are indebted to O. G. Brandt for the loan of samples provided by Dr. H. J. Anderson of Battelle-Northwest.

⁷ A. Arrott and J. E. Goldman, Phys. Rev. **108**, 948 (1957).

Temperature-Dependent Polarizabilities in Paraelectric BaTiO_3 and SrTiO_3 †

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(Received 27 June 1966; revised manuscript received 28 December 1966)

A generalized internal-field theory of the pressure, temperature, and composition dependence of the dielectric constant is presented which allows the independent determination of *two* polarizabilities from experimental data. The model is shown to involve the total polarizabilities of *A* and *B* and the electronic polarizability of *O* for the perovskite lattice, ABO_3 , so that certain comparisons with optical data can be made via the oxygen polarizability. The three polarizabilities are determined parametrically using experimental data for BaTiO_3 (120 to 350°C) and SrTiO_3 (−150 to 0°C), and it is found that acceptable polarizability solutions are limited to a surprisingly narrow “band” for each polarizability. These solutions are then used to determine the explicit temperature and volume dependences of the polarizabilities in both crystals. For BaTiO_3 it is concluded that the explicit temperature dependence of the oxygen polarizability is very weak, and that the major contribution to $(\partial\epsilon/\partial T)_p$ is the explicit dependence of the Ti polarizability (ionic) on temperature (i.e., the Slater model). For SrTiO_3 , the data are interpreted as requiring an explicit temperature dependence of the oxygen polarizability, in contrast to the BaTiO_3 case, and all contributions to $(\partial\epsilon/\partial T)_p$ for SrTiO_3 are found to be of equal importance, also in contrast to BaTiO_3 .

I. INTRODUCTION

ONE convenient description of the dielectric constant (or refractive index) of ionic crystals is in terms of the polarizabilities of the ions and the local fields at these ion sites: One places polarizable-point dipoles at the lattice sites and considers the interaction of these dipoles with one another and with an external field. In this formulation, the polarizabilities are the solutions of an eigenvalue problem in the general case, but only *one* polarizability can be determined, relative to the other polarizabilities which must be given. This

is a situation similar to determining ionic radii, and self-consistent tabulations of polarizability data derived from dielectric data in this fashion have been reported in the literature.^{1,2}

A more complex problem results when one considers the temperature (or pressure) dependence of the dielectric constant in this polarizable-point-dipole approximation. There are two contributions in this case, one strictly a volume effect (i.e., through thermal expansion or compressibility), and the other the explicit dependence of the polarizabilities on volume or temperature. This second contribution is important,

† A portion of this research was presented at the International Conference on Ferroelectricity, Prague, 1966 (to be published).

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¹ J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

² K. Fajans and G. Joos, Z. Physik **23**, 1 (1924); see also Refs. 16 and 17.