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THE MAGNETOCRYSTALLINE ANISOTROPY OF GALLIUM AND ALUMINIUM SUBSTITUTED MAGNETITE

By R. F. PEARSON,

Résumé. — Les valeurs de la constante d’anisotropie $K_1$ ont été mesurées de 120 °K à 400 °K par la méthode de torsion, pour sept cristaux de magnétite substituée par du gallium ou de l’aluminium. La distribution ionique de ces cristaux a été déterminée avec soin à l’aide d’autres mesures, physiques et chimiques, et une analyse préliminaire des résultats a été faite, afin de décider de l’importance relative des mécanismes qui contribuent à la variation anormale de l’énergie d’anisotropie de la magnétite.

Abstract. — Values of $K_1$, the first order anisotropy constant, have been measured by torque methods from 120 °K to 400 °K for seven crystals of gallium or aluminium substituted magnetic. The ionic distribution in these crystals has been carefully determined from other physical and chemical measurements and a preliminary analysis has been made of the results to decide the relative importance of the mechanism contributing to the anomalous variation of the anisotropy energy in magnetic.

Introduction. — In recent years several mechanisms have been proposed to explain the observed anisotropy energies in ferrites. The relative importance of the three principal mechanisms, dipole-dipole interaction, anisotropic exchange interaction, and interaction between the individual magnetic ions and the crystalline electric field, has been investigated by Yosida and Tachiki (1957) and Wolf (1958) for Ni, Co, Fe and Mn-ferrites, although the lack of suitable experimental data on stoichiometric ferrite crystals makes any exact comparison with theory very difficult. The aim of the present work was to study the origin of the magnetocrystalline anisotropy in magnetite ($Fe_3O_4$) as this shows a rather anomalous variation with temperature. Previous workers (Bickford (1950)) have reported that the first order anisotropy constant $K_1$ is negative at 300 °K, passes through zero at about 130 °K (the easy direction of magnetization changes from [111] to [100]) and at 119 °K a crystallographic transition occurs, the crystal symmetry reducing from cubic to orthorhombic owing to the long range ordering of ferric and ferrous ions on the octahedral lattice sites, e.g. Verwey and Haayman (1941). Bickford (1957) has shown from anisotropy measurements on cobalt substituted magnetite that the change in sign of $K_1$ in magnetite is not due to the presence of cobalt impurity and one might therefore assume the change is caused by short range ordering of $Fe^{2+}$ and $Fe^{3+}$ ions at temperatures above the transition point. However Rado (1958) has measured the anisotropy constants of some mixed crystals of magnesium ferrite and magnetite and suggests that $Fe^{3+}$ ions give contributions of opposite sign to the anisotropy depending on whether they occupy the tetrahedral or the octahedral sites, thus providing support for the crystal field theory which predicts similar results according to Yosida and Tachiki (1957). In this paper results are presented of anisotropy measurements made on substituted single crystals of magnetite of nominal composition $Ga_xFe_{3-x}O_4$ (where $x = .08, .14, .27, .36$) and $Al_yFe_{3-y}O_4$ (where $y = .10, .21$). Substitutions of gallium and aluminium were chosen because of their tendency to

### TABLE 1

<table>
<thead>
<tr>
<th>Type of crystal</th>
<th>Chemical Analysis</th>
<th>Lattice constant</th>
<th>Resistivity</th>
<th>Temperature Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>$Fe^{2+}Fe^{3+}O_4$</td>
<td>8.396 ± .005 Å</td>
<td>5 × $10^{-3}$ ohm cm</td>
<td>114 °K</td>
</tr>
<tr>
<td>MGa1</td>
<td>$Fe^{2+}Ga^{3+}Fe^{3+}O_4$</td>
<td>8.393 ± .005 Å</td>
<td>7 × $10^{-3}$ ohm cm</td>
<td>127 °K</td>
</tr>
<tr>
<td>MGa2</td>
<td>$Fe^{2+}Ga^{3+}Fe^{3+}O_4$</td>
<td>8.390 ± .005 Å</td>
<td>10^{-2} ohm cm</td>
<td>—</td>
</tr>
<tr>
<td>MGa3</td>
<td>$Fe^{2+}Ga^{3+}Al^{3+}O_4$</td>
<td>8.388 ± .005 Å</td>
<td>1 × $10^{-2}$ ohm cm</td>
<td>—</td>
</tr>
<tr>
<td>MGa4</td>
<td>$Fe^{2+}Ga^{3+}Al^{3+}O_4$</td>
<td>8.385 ± .005 Å</td>
<td>1.5 × $10^{-2}$ ohm cm</td>
<td>—</td>
</tr>
<tr>
<td>MAI1</td>
<td>$Fe^{2+}Al^{3+}Fe^{3+}O_4$</td>
<td>8.378 ± .005 Å</td>
<td>9 × $10^{-3}$ ohm cm</td>
<td>&lt; 80 °K</td>
</tr>
<tr>
<td>MAI2</td>
<td>$Fe^{2+}Al^{3+}Fe^{3+}O_4$</td>
<td>8.374 ± .005 Å</td>
<td>1 × $10^{-3}$ ohm cm</td>
<td>—</td>
</tr>
</tbody>
</table>
occupy preferentially the tetrahedral or octahedral sites respectively and thus should enable the effect of Fe$^{3+}$ ions on the different sites to be studied separately to see if they are in fact responsible for the anomalous variation of the anisotropy energy in magnetite.

**Preparation and analysis of crystals.** — Large single crystals (about 4 cm long by 1 cm diameter) of composition Ga$_{2-}$Fe$_{3-}O_4$ and Al$_y$Fe$_{3-}O_4$ have been grown from the melt by other workers in these laboratories using the method described by Smiltens (1952). Starting materials were high purity oxides (specpure), containing less than .001 % cobalt impurity. Representative slices of each crystal were chemically analysed, and the crystal lattice constants determined from x-ray powder photographs. The specimens used in the present investigation were taken from slices adjacent to parts for which the chemical analysis was known and were ground into the shape of small spheres (about 1.5 mm diameter) using standard techniques e.g. Bond (1951). The spheres were then transferred to thin glass rods in the appropriate crystallographic orientation as determined by X-ray back-reflexion Laue photographs. Details of the chemical composition of the samples are given in table I. The volume of the specimens was determined from the measured weight and values of the X-ray density calculated from the chemical analysis and the lattice constant. It can be seen from table I that in M1, nominally a magnetite composition, the ratio of trivalent to divalent iron is slightly greater than two, which indicates the presence of octahedral vacancies. According to Verwey and Haayman (1941) this would tend to depress the temperature at which the transition occurs in magnetite. Measurements of the initial permeability on single crystal toroids cut from the same crystals as M1 and MGa1 showed transitions at 114 °K and 107 °K respectively compared with the value of 119 °K for stoichiometric magnetite. For a crystal of composition MA1 the transition was not detected at temperatures down to 80 °K, confirming that Al$^{3+}$ ions tend to occupy the octahedral sites preferentially and thus suppress the long range ordering of Fe$^{2+}$ and Fe$^{3+}$ ions. Further information on the chemical composition of the crystals was gained from some preliminary measurements of resistivity on the original single crystal ingots. The values of the resistivity at room temperature are shown in table I.

**Anisotropy measurements.** — The anisotropy constants were measured by the torque method. For a cubic crystal magnetized to saturation in a (100) plane the torque is given by:

$$J_{100} = - (K_1 \sin \theta)' / 2$$

where $K_1$ is the first order anisotropy constant and $\theta$ is the angle between the direction on magnetization and the [100] direction.

The crystals were mounted such that the direction of magnetization could be rotated in the (100) plane and the torque curves measured using the apparatus shown in figure 1. In order that a
large number of measurements could be made over a wide temperature range the equipment was made automatic in operation such that the torque curves were plotted directly on an X-Y recorder, in a manner similar to that described by Penoyer (1956). Torques in the range 0-500 dyne cm could be measured to an accuracy of 1 dyne cm. The apparatus allowed calibration with the specimen in situ and at all temperatures. Fuller details of the equipment will be described elsewhere. The values of $K_1$ were determined from the peak heights of the torque curves. Some preliminary measurements were made of torque curves in a (110) plane, which required a Fourier analysis to determine the values of $K_1$ and $K_2$ owing to the presence of an additional sin$2\theta$ component presumably due to a shape effect in the sample. All the measurements were made in magnetizing fields of 12,000 oersteds and by suitable methods of controlling the temperature of the specimen torque curves were measured at 15 °K intervals over the temperature range 120 °K-400 °K.

**Experimental results.** — The experimental values of $K_1$ are plotted against temperature for the crystals M1, MGa1, MGa2, MGa3, MGa4 in figure 2 and the crystals M1, MA11, MA12 in figure 3. The experimental error in $K_1$ is thought to be less than $1.5 \times 10^3$ ergs/cc, although difficulties in temperature control may introduce...
errors of up to 3 oK in the points plotted below 150 oK. The value of \( K_1 \) at 300 oK for the crystal M1 was \(-12.8 \times 10^4\) ergs/cc compared with the value of \(-13.1 \times 10^4\) ergs/cc reported by Bickford (1957) for stoichiometric magnetite. The effect of increasing substitutions in magnetite is seen to lower the temperature at which \(|K_1|\) passes through a maximum from 230 oK for M1 to 170 oK for MGa4. Similar behaviour in a single crystal of magnetite containing 50 % of magnesium ferrite has been found by Rado (1958) the value of \(|K_1|\) showing a maximum at 180 oK. In order to determine the distribution of the magnetic ions between the tetrahedral and octahedral sites, measurements of the saturation magnetization at low temperatures have been made by Dr. F. W. Harrison of these laboratories. The extrapolated values of the magnetic moment are shown in Table 2, together with the probable ionic distribution corresponding to these values using the theory of ferrimagnetism due to Néel (1948). Further saturation magnetization measurements are being carried out on all the samples over the whole temperature range up to the Curie point. Finally it should be pointed out that further anisotropy measurements are being made on crystal positions containing aluminium as a crystal of nominal composition MA12 was found to exhibit rather unusual behaviour. The torque curves were found to vary with applied field, the torque decreasing in fields above 10,000 oersteds. The results plotted for MA12 in this paper were obtained from a specimen which gave normal torque curves, the torque remaining constant in fields above 8,000 oersteds.

**Discussion of results.** In figure 4 the variation of \( K_1 \) with temperature is shown for all the samples referred to in this paper in order that the relative effects of the gallium and aluminium substitutions may be observed. The analysis of the results is complicated by the fact that only 70 %
to 80% of the gallium and aluminium substituted ions go into the tetrahedral and octahedral sites respectively, according to table 2, so that for the crystals under investigation magnetic ions on both A and B sites are replaced simultaneously. At temperatures above 350 °K the effect of large substitutions (greater than 0.1 mol) in magnetite is to reduce the value for $K_1$ but below 150 °K $K_1$ is increased. This would tend to confirm that short range ordering of Fe$^{2+}$ and Fe$^{3+}$ ions in magnetite above the transition point causes $K_1$ to decrease and eventually to change sign because the suppression of the ordering when non-magnetic ions or vacancies are introduced into the octahedral sites, would increase $K_1$. However following this reasoning one would expect the values of $K_1$ for aluminium substituted crystals to show very large increases owing to the tendency of Al$^{3+}$ to occupy the octahedral sites preferentially, whereas at 150 °K the value of $K_1$ for MA11 (−9.7 × 10$^3$ ergs/cc) is much lower than for MGa3 (−12.0 × 10$^3$ ergs/cc) although it can be seen from table 2 they each contain approximately the same number of non-magnetic ions in the octahedral sites. A preliminary analysis of the results above 300 °K has been made to test the validity that the anisotropy contributions per magnetic ion are additive. Although it seems possible to derive satisfactory values for MGa2, MGa3, MGa4 using this model (Fe$^{3+}$ ion on A sites is found to give a negative contribution approximately three times as large as the positive contribution of a Fe$^{3+}$ ion on a B site) it is emphasized that satisfactory agreement for all the samples is not obtained. In this respects it is noted that as all the crystals possess different Curie temperatures, due to the effect of non-magnetic substitutions, a true comparison can only be made between $K_1$ values plotted as a function of $(T/\theta)$ where $\theta$ is the appropriate Curie temperature. The Curie temperatures of these ferrites are at present being measured. It seems that the curves of $K_1$ plotted vs $(T/\theta)$ tend to be displaced such that the peak values of the anisotropy tend to nearly coincide. A more detailed analysis of these results will be presented in the near future.

**Conclusions.** — Values of $K_1$ the first order cubic anisotropy constant have been determined over the temperature range 120-400 °K for seven crystals of gallium or aluminium substituted magnetite. The ionic distribution in these crystals has been carefully determined from other physical and chemical measurements and a preliminary analysis has been made of the results to determine the relative importance of the mechanisms contributing to the anomalous variation of the anisotropy energy in magnetite.

**Acknowledgements.** — The author wishes to thank Dr. K. Hoselitz under whose direction this work was carried out an various members of the Mullard Research Laboratories for their co-operation particularly: Dr. F. W. Harrison for the magnetic moment measurements; Mrs. S. Misso for the X-ray analysis; Mr. R. Dench for the construction of apparatus; Mr. R. Cooper for assistance in its operation; Mr. R. Crompton of the Crystal Growing Section and finally Mr. W. P. Osmond for valuable discussions.

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Verwey (E. J. W.), Haayman (P. W.), Physica, 1941, 8, 979.

**DISCUSSION**

Mr. Wolf. — I should like to point out the danger of comparing quantities like $K_1$ on different samples in terms of reduced temperatures $(T/\theta)$ involving the Curie points of the samples. The true parameters involved are the relative magnetizations of the different sublattices and it would be necessary to calculate these from the total magnetic moment measurements using Néel’s analysis.

Mr. Pearson. — I would agree with Dr. Wolf and add that we intend to determine the relative sublattice magnetizations, when the measurements of the $(\sigma, T)$ curves up to the Curie point are completed.

Mr. Dammann. — Which method did you use to determine the distribution of ions on octahedral and tetrahedral sites?

Mr. Pearson. — We deduced the data from measurements of saturation magnetization.