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MAGNETIC PROPERTIES OF PURE AND CHROMIUM AND SCANDIUM-SUBSTITUTED SINGLE CRYSTALS OF HEMATITE

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The magnetic properties of pure hematite single crystals and of hematite single crystals in which part of the iron ions is replaced by chromium ions are investigated. It is found that the addition of scandium or chromium broadens the temperature range of the existence of weak ferromagnetism. The spontaneous magnetization of each of the crystals grown is determined.

HEMATITE (α-Fe_2O_3) has a rhombohedral lattice (space group $R\bar{3}c$); the spins of its iron ions above the Morin point (263°K) lie in the basal plane, the angle between them differing little from 180°. This small deviation from antiparallelism leads to the existence of weak ferromagnetism. Below the Morin point the spins turn along the trigonal axis and are located antiparallel to one another; as a result of this hematite goes over to the antiferromagnetic state. It is well known[1] that small additions to hematite of ions of aluminum, gallium, and titanium extend the region of the existence of weak ferromagnetism shifting the Morin point towards the region of lower temperatures.

We have grown and investigated the magnetic properties of single crystals of pure hematite and hematite a part of whose iron ions have been substituted by chromium ($0.9Fe_2O_3$–$0.1Cr_2O_3$) and scandium ions ($0.95Fe_2O_3$–$0.05Sc_2O_3$).

The pure hematite crystals were synthesized in a flux of (Bi_2O_3 + Na_2CO_3).[2] The addition of chromium oxide to the hematite led to a reaction of the Cr_2O_3 with the Na_2CO_3. Therefore these single crystals were grown from a solution of a mixture of the Fe_2O_3 and Cr_2O_3 oxides in a melt of pure Bi_2O_3 without the addition of sodium carbonate. The ratio of solute to solvent was taken to be 3 : 1. The crystals were grown in a platinum crucible. The crucible was heated in a furnace for 9–10 hours up to 185°C, was kept at that temperature for 3 hours and cooled down to 800°C at a rate of 8 deg/hour.

The single crystals with the scandium oxide were grown in principle by the same method.

The obtained crystals were washed of the flux by boiling them in dilute nitric acid. The grown crystals are black and have a mirror-like metallic luster. They grow preferentially in the form of platelets with thicknesses up to 2 mm.

The magnetic properties of the crystals of pure hematite and of hematite with substitutions were investigated by the torque method. This method is suitable for investigating weak ferromagnetism. For weak ferromagnets the magnetization of the crystals σ in a magnetic field H is related with the spontaneous magnetization σ_0 by the following relation:

$$\sigma = \sigma_0 + \chi H, \tag{1}$$

where χ is the susceptibility of the crystal. The magnetic energy is $E = \sigma \cdot H$ and the torque L in a plane perpendicular to the basal plane will be expressed by the following relation:

$$L = -\frac{\partial E}{\partial \vartheta} = (\sigma_0 H + \chi H^2)\sin\vartheta. \tag{2}$$

Here ϑ is the angle between the c axis and the direction of the magnetic field.

Figure 1 shows the torque curves of the investigated crystals [unlike in formula (2) where L is measured in erg/g, on the graphs L is in erg/cm^3]. The torque curve of pure hematite at 293°K (curve 1) is well described by Eq. (2), that is it is a first-order sinusoid. At a temperature below the Morin point the curve goes over in accordance with the theory into a second-order curve (curve 2 at 77°K). The crystal goes over into the antiferromagnetic state. The addition of scandium (curve 3) or chromium (curve 4) extends the temperature range within which weak ferromagnetism exists. Both at 77°K and at 293°K the crystals are weakly ferromagnetic, the magnitude of the spontaneous magnetization being the same at these two temperatures (the torque curves are identical).

In the basal plane the spontaneous magnetization vector rotates practically isotropically. The magnetic anisotropy constant in this plane is in any case less than 10^2 erg/cm^3 for each of the investigated crystals.

A confirmation of the fact that we are dealing with weak ferromagnetism is Fig. 2 in which we present the dependence of the maximum torque L_{max} on the magnitude of the applied magnetic field H. This torque de-

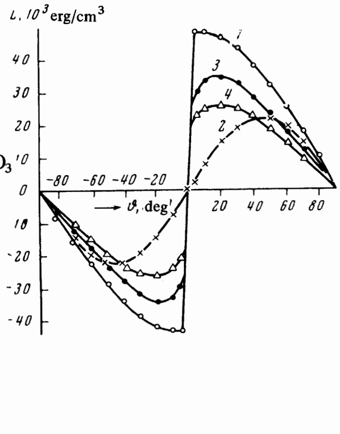

FIG. 1. Torque curves: 1 – for α-Fe_2O_3 at 293°K; 2 – α-Fe_2O_3 at 77°K; 3 – for $0.95Fe_2O_3$–$0.05Sc_2O_3$ at 293°K; 4 – for $0.9Fe_2O_3$–$0.1Cr_2O_3$ at 77 and 293°K.

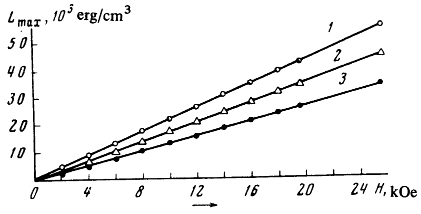

FIG. 2. Dependence of the maximum torque on the magnitude of the magnetic field: 1 – for α-Fe_2O_3 at 293°K; 2 – for $0.95Fe_2O_3$–$0.05Sc_2O_3$ at 77 and 293°K; 3 – for $0.9Fe_2O_3$–$0.1Cr_2O_3$ at 77 and 293°K.

pends linearly on H, indicating thereby that the susceptibility χ is small and can be neglected.

It remains for us to evaluate the magnitude of the spontaneous magnetization $\sigma_0 = L_{max}/H$ for each composition. For pure α-Fe_2O_3 at 293°K we have $\sigma_0 = 0.42$ gauss-cm^3/g (which corresponds to the data in the literature). For crystals of the composition $0.95Fe_2O_3$—$0.05Sc_2O_3$ we have $\sigma_0 = 0.34$ gauss-cm^3/g (at 77 and 293°K), and for crystals of the composition $0.9Fe_2O_3$—$0.1Cr_2O_3$ we have $\sigma_0 = 0.25$ gauss-cm^3/g (at 77 and 293°K).

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[1] P. J. Besser, A. H. Morrish, and C. W. Searle, Phys. Rev. **153**, 632 (1967).

[2] R. A. Voskanyan and I. S. Zheludev, Kristallografiya 12, 539 (1967) [Sov. Phys. Crystallogr. **12**, 473 (1967)].