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Studies of magnetic axis switching phenomenon in magnetite

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Abstract

The results of magnetic and structural studies of magnetic easy axis switching in magnetite are presented. This phenomenon was first observed after the easy axis was established by the in-field cooling across the Verwey transition. Although the subsequent application of magnetic field at low temperatures along certain <1 0 0> is almost as effective in establishing the easy axis as field cooling, the repeated easy axis redirection below T_V causes the field required to switch the axis to become lower. We have also shown that the change of magnetic easy axis is reflected in the change of crystallographic *c* direction. Finally, the energy required to switch the axis was calculated and was found comparable to the characteristic energy of the Verwey transition.

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1. Introduction

It is well known that in magnetite below the Verwey transition temperature $T_V = 124$ K some processes occur that lead to abrupt change of many physical properties, in particular, the crystal symmetry lowers from cubic ($Fd3m$) to monoclinic Cc. In spite of more than 70 years after the Verwey transition was discovered, it still attracts attention [1–3] due the vital problem of possible charge ordering at the metal-to-insulator transition. In the paper, the results of observation of one aspect of crystal structure change from cubic to monoclinic was presented: the magnetic easy axis switching phenomenon (AS).

Due to the change of structure at T_V, each of high temperature cubic <1 0 0> directions may become the low temperature monoclinic *c*-axis, doubled in comparison to the cubic lattice constant. As a result, the material breaks into several structural domains unless the external magnetic field $B > 2$ kGs along particular [0 0 1] is applied while cooling through the transition. This particular direction will also become the magnetically easy axis. Once the magnetic easy axis has been established by the above procedure and the magnetite sample is magnetized along other <1 0 0> direction at temperatures lower than T_V, a reorientation of magnetic moments, i.e. axis switching, may take place and this <1 0 0> direction becomes a new easy axis [4,5]. The magnetic field required to switch the axis fulfils the relation:

$$B = cT\,e^{U/kT} \tag{1}$$

with the activation energy $U = 0.033$ eV [4].

Quite early on Verwey suggested that at high temperatures the material could be viewed as a disordered electron system with Fe^{3+} ion core and "additional" electrons (forming Fe^{2+} ions) resonating between adjacent octahedral positions. The transition is, thus, the freezing of those resonating electrons, whereby Fe^{2+} and Fe^{3+} cations order on certain octahedral positions. Recently the orthodox meaning of charge ordering concept was questioned [1,3] and non-complete charge disproportionation [2], or octahedral iron dimmers rather than separate, well-defined Fe^{2+} and Fe^{3+} cations, are proposed [6] to form below T_V. Nevertheless the description of the Verwey transition as some cation orientation is still attractive. It is thus tempting to explain the axis switching by Fe cations reorientation under the magnetic field to minimize their energy. That is, either the electron hopping to the new positions would take place if charge ordered

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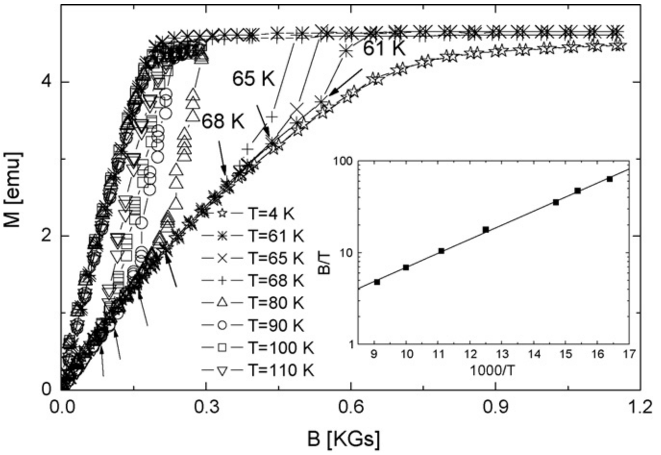

Fig. 1. Results of "full heat treatment" experiments: $M(B)$ isotherms along [0 1 0] were measured after field cooling in $B = 10$ kGs along [0 0 1] across T_V (easy axis establishing). As long as the axis switching does not occur, $M(B)$ is reversible and typical for an unspecified magnetic direction (e.g. stars for 4.2 K). The arrows show the onset of axis switching.

low temperature state exists, or Fe dimmers change orientation if dimmer model is true. In any case, this requires the simultaneous reorientation of magnetic and crystallographic (in particular, the monoclinic *c*) axes which was experimentally proved and reported recently [7]. In the present paper, those studies are extended to lower temperatures and it is shown that the field required to switch the axis depends on sample's history. We also show that the energy of field required to change the easy magnetic axis, i.e. also to redirect the monoclinic *c*-axis, is comparable to the characteristic energy of the Verwey transition.

2. Experimental

The samples were single crystals of magnetite skull melter grown from 99.99% pure Fe_2O_3 and annealed for stoichiometry. Magnetization measurements were performed on VSM (Lake Shore 7300) at magnetic field up to 10 kGs and in the temperature range 4.2 K-T_V. For magnetization studies, the sample was of cylindrical shape (the vertical, cylinder, axis was along [1 0 0]) glued to the measurement rod in such a way that two other directions of <1 0 0> type could be aligned along external magnetic field (see the inset of Fig. 2 for experimental arrangement) provided by the electromagnet. Crystal structure experiments were done on the four-circle KM4 diffractometer with graphite-monochromatized Mo Kα radiation and cold nitrogen gas cooling system (Oxford Cryosystems).

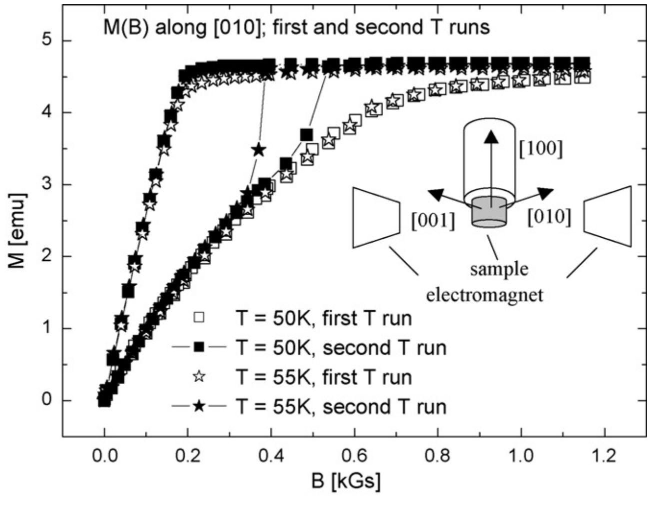

Fig. 2. Checking the field required to switch the axis after it was established at $T < T_V$. In each case, $M(B)$ was measured along [0 1 0] and the field of 10 kGs along original [0 0 1] was applied afterwards to reestablish original [0 0 1] easy axis. Only the selected results from two subsequent temperature runs are shown. Note that while for $T = 50$ K the field of 10 kGs does not switch the axis in the first run (open squares), a field of 4 kGs is required to make AS in the second T run (full squares). In the inset, the experimental arrangement is shown.

It was first intended to observe the magnetic axis switching in a wide temperature range and to precisely establish the lowest temperature at which the field of 10 kGs can switch the easy axis. The results are presented in Fig. 1 and in each experiment the sample was first field cooled (FC; $B = 10$ kGs, along [0 0 1]) across T_V to the specified temperature, the $M(B)$ was measured along this direction (the easy axis direction) and the sample was rotated 90° and $M(B)$

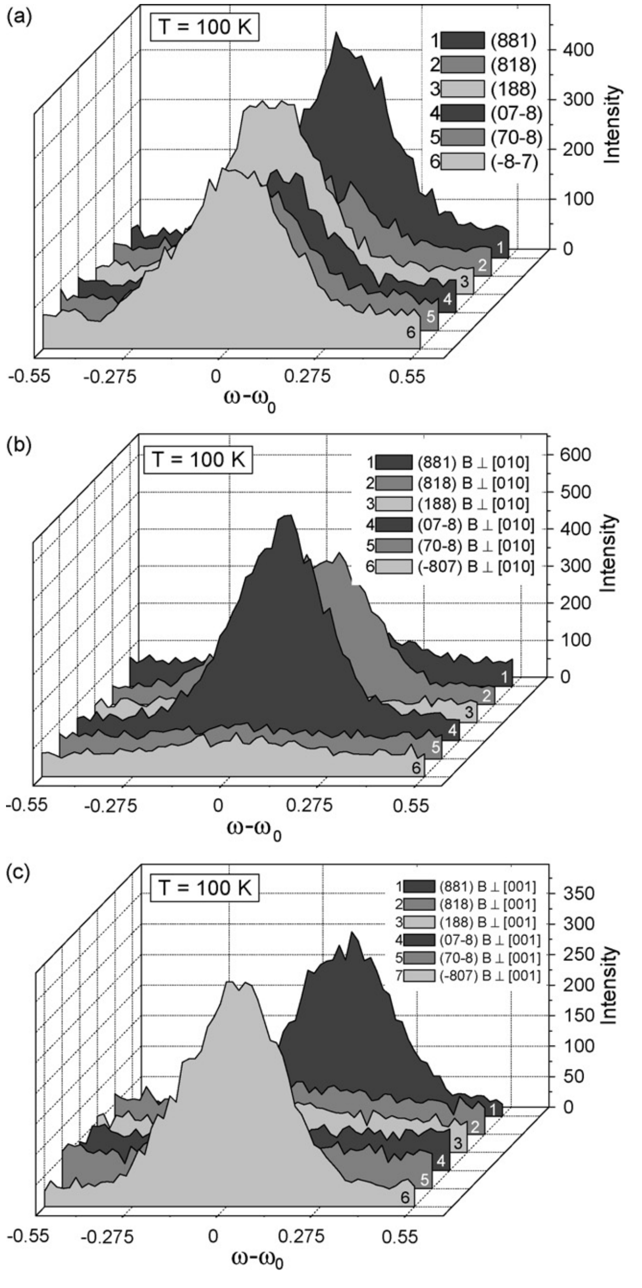

Fig. 3. Peak profiles of <8 8 1> and <0 7 −8> reflections (ω scan around peak position ω_0) after ZFC (zero field cooling) (a) and after the field was applied along [0 1 0] (b) or [0 0 1] (c). Note, that due to experiment geometry the field could not be applied along [1 0 0].

was measured along [0 1 0] (which is not any specific magnetic direction). At low T, up to ca. 50 K, the $M(B)$ looked like the typical curve for magnetically intermediate direction (as for 4.2 K; stars) and was reversible. For higher temperatures (e.g. for $T = 61$ K shown in Fig. 1), the easy axis may be switched by magnetic field and demagnetization $M(B)$ curve was typical for the new easy axis along [0 1 0]. The values of fields required to switch the axis after these "full heat treatment" experiments (FC from above T_V along [0 0 1]) are shown in the inset of Fig. 1 together with the fit to the formula (1).

Similar studies (i.e. checking the fields required to switch the axis) were then attempted but the easy axis was set at low temperature. It was previously found [7] that application of field of at least 2 kGs along, e.g. [0 0 1] direction at 80 K can establish the easy magnetization direction (along this [0 0 1]) equally well as cooling down from high temperatures. Here, the sample was field-cooled with B along [0 0 1] and $M(B)$ was measured along [0 1 0] every few K ("first T run"). After each measurement, the field of 10 kGs along original [0 0 1] was applied to the sample to reestablish original [0 0 1] easy axis in case AS occurred. The results are shown in Fig. 2 (open symbols) for two representative temperatures. The switching fields are lower comparing to those shown in Fig. 1 and the relevant energy calculated from the formula (1) is 89 K, i.e. considerably lower than that calculated from "full heat treatment" experiments.

After the highest temperature for this experiment was reached (71 K), the sample was cooled down again and re-measured at few temperatures ("second T run"). The results for both T runs at two temperatures (50 K, where hardly any changes to the $M(B)$ curve were seen for the "first T run" and 55 K, for which the switching field from the first T run was ca. 10 kGs) are shown as the examples. It is clear that in the second T run the fields needed to switch the axis are still lower (i.e. also much lower than in "full heat treatment" experiments). Apparently, T cycling "weakens" the sample magnetically.

It was now interesting to find out if the relaxation of magnetic easy axis is accompanied by the simultaneous change of monoclinic c-axis. In other words, we wanted to check if the application of magnetic field can change the intensity of superstructure peaks, related to the doubling of c-axis, i.e. of <8 8 1> or <8 0 7> types. The sample was first cooled down to 100 K and the omega scans of (8 8 1), (8 1 8), (1 8 8) and (0 7 −8), (−8 0 7), (7 0 −8) reflections were measured. With the absence of magnetic field the intensities within each type of reflections should be comparable (see Fig. 3a). The field of $B \sim 3$ kGs (generated by the set of NdFeB magnets) was now applied to the sample roughly in [0 1 0] (Fig. 3b) and [0 0 1] (Fig. 3c) directions (cubic indexing). Each time the experiment was repeated the peak profiles from two sets of reflections were measured. It is clear that the peak intensities change in accordance with the field direction. We have thus shown that the application of magnetic field simultaneously rearranges the direction of easy magnetic axis and the monoclinic c-axis.

3. Discussion

The most important outcome from the presented studies is that switching of the magnetic axis is equivalent to changing the monoclinic distortion of the cubic high temperature structure of magnetite. The results of the linear fit from Fig. 1 gave the energy required to switch the axis as $U/k_B \sim 153$ K, i.e. close to the characteristic energy of the Verwey transition. In other words, applying the magnetic field enables to manipulate those species (possibly 3d iron electrons) that cause symmetry lowering and the Verwey transition simultaneously. It was also noticed that the way the sample reacts to the magnetic field depends on it's history: the same experiments repeated after several field treatment and heating the sample to around 70 K result in lower magnetic field required to switch the axis. Similar, preparation dependent, phenomena were observed in other experiments [8]. All those facts and the conjecture that axis switching is deeply involved with the transition suggest that one should check the transition temperature after extensive field cycling at temperatures below T_V. Although in several reports [9,10] some dependence of the Verwey transition temperature on magnetic field was found which might suggest T_V dependence upon field cycling, more dedicated studies are needed.

In conclusion, we have shown that the magnetic easy axis switching that can be caused by the application of magnetic field is accompanied by the relaxation of low temperature structure. It was also found that the extent of this phenomenon depends on sample's history in the sense that frequent magnetic field cycling lowers the field required to change the magnetic easy axis. The implications of these findings to the Verwey transition temperature were discussed.

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