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X-ray studies of $Fe_{3-x}Me_xO_4$, Me = Zn, Ti and Al; the impact of doping on the Verwey transition

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Abstract

We have performed structural X-ray studies of $Fe_{3-x}Me_xO_4$, where Me = Zn, Ti and Al in temperature range 70–300 K. Very small doping by Zn, Ti or Al, studied here, greatly disturbs this strongly correlated electron–phonon system changing the Verwey transition temperature as well as transition character from discontinuous to continuous one. We discuss temperature dependence of lattice parameters determined by the Rietveld analysis for specimens showing different types of transition to find out whether the transition is already prearranged at high temperatures e.g. suggested by our elastic constant data. We also compare the change of the structure at the Verwey transition for these two classes of materials.

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Keywords: Magnetite; Verwey transition

1. Introduction

Magnetite Fe_3O_4, characterizes the spectacular phase transformation at $T_V \approx 120$ K, known as the Verwey transition, at this temperature discontinuous anomalies exist in many physical properties (e.g. resistivity and heat capacity [1]) that clearly show the first-order character of this phase transformation. This transition is usually believed to originate from ionic ordering of the Fe ions at the octahedral sites e.g. Ref. [2] in accordance with Mott–Hubbard theory of highly correlated electron systems. However, some recent measurements question the freezing electron picture [3] suggesting, instead of the charge ordering into two (Fe^{2+}–Fe^{3+}) ionic states, some charge

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segregation on the inequivalent Fe positions of the low temperature phase with the Fe valence remaining unaltered. The charge density and also the way the octahedral sublattice is perturbed may be finely tuned by means of different substituents as with Zn, Ti, and Al. These are nonmagnetic dopants that enter different lattice positions: Zn^{2+}—tetrahedral, Ti^{4+}—octahedral, and Al^{3+}—both. Moreover, even very small substitution for iron lowers the transition temperature and the nature of the Verwey transition is changed from first order to the continuous one [1].

The transition is also reflected in the change of the crystal structure from high-temperature cubic (Fd3 m) to presumably low-temperature monoclinic (Cc). It is, therefore, interesting to check how the low-temperature structural distortion changes with doping and if the change of the transition character is distinguished by the structural characteristics for different dopants. Here, the problem has been addressed by X-ray diffraction measurements.

2. Experimental

Single crystalline $Fe_{3-x}Me_xO_4$, Me = Zn, Ti and Al, were grown by the skull melter technique [4]. The transition temperature (i.e. sample quality) was checked by AC susceptibility.

X-ray diffraction (XRD) measurements were performed in the temperature range 70–300 K on a Siemens D5000 diffractometer equipped with the OXFORD continuous flow cryostat, and a rear graphite monochromator using CuK_α radiation. The complete XRD scans ($16^\circ \leqslant 2\theta \leqslant 114^\circ$) were generally collected at 300, 70 K and, in selected cases, at some other temperatures to clarify structural problem. The XRD patterns were fitted using FULLPROF [5] program assuming the pseudo-Voight function for peak shape and polynomial function for the background intensity.

3. Results and discussion

From our measurements, X-ray diffraction patterns of $Fe_{3-x}Me_xO_4$, where Me = Zn, Ti and Al, compounds were indexed between 300 K and T_V on Fd3 m space group. However, below T_V the patterns were indexed in the rhombohedral symmetry (space group $R\bar{3}m$), instead of the actual monoclinic symmetry to avoid problems with strong overlap of peaks that are not observed but are permissible by much lower symmetry. Since no accurate model of the low-temperature complex structure of $Fe_{3-x}Me_xO_4$ compounds is available in the literature the pattern matching method was applied (refinement without structural model) to refine these patterns and obtain the most reliable values of the lattice parameters.

Monoclinic unit cell parameters were then calculated from fitted rhombohedral unit cell data. The temperature dependence of monoclinic angle β_M for samples with different Ti and Al concentration exhibiting first- and second-order type transitions are shown on Fig. 1.

These results are consistent with earlier data for $Fe_{3-x}Zn_xO_4$ [6] showing the diminution of the lattice distortion and transition temperature together with the change of the transition character irrespective of the type of dopant. Also universal behavior is visible in the temperature dependence of lattice parameters presented in Fig. 2.

Above T_V, lattice parameters decrease in unique way reaching minimum close to transition temperature. Below, the transition lattice parameters are constant and no thermal contraction is observed. Also rhombohedral distortion remains

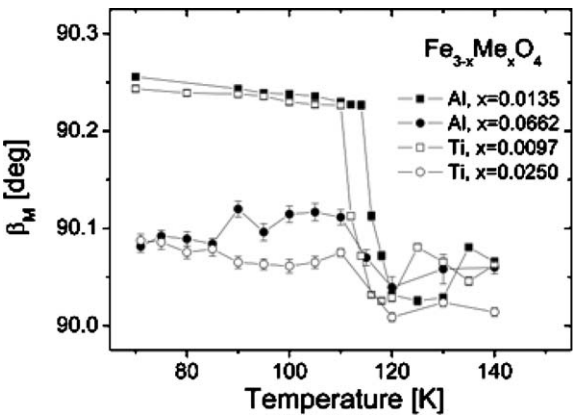

Fig. 1. Temperature dependence of monoclinic β_M angle for $Fe_{3-x}Me_xO_4$, where Me = Ti and Al samples.

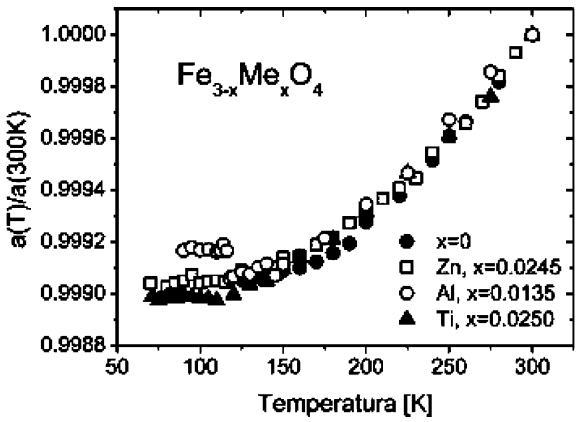

Fig. 2. The temperature dependence of lattice parameters.

almost unchanged (Fig. 1). This fully agrees with our earlier studies of zinc ferrites [6]. This behavior is particularly interesting since various substituents change lattice in a different way. Cation radius of Al^{3+} (53pm) is smaller than that for Fe^{3+} (64pm) hence the volume of elementary cell diminishes with Al concentration, whereas doping with both other elements increases the volume of elementary cell (cation radiuses are respectively comparable Ti^{4+} (61pm) or larger Zn^{2+} (74pm) than Fe^{3+}). Keeping in mind that doping with Zn^{2+}, Al^{3+}, and Ti^{4+} should also differently affect charge density the observed universal compositional and temperature dependence of lattice parameters for $Fe_{3-x}Me_xO_4$, Me = Zn, Ti and Al, suggest intimate connection between the Verwey transition and crystal lattice properties.

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