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HEAT CAPACITY AND ELASTIC CONSTANTS OF $Fe_{3-x}Zn_xO_4$ IN THE VICINITY OF THE VERWEY TRANSITION

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The results of the heat capacity and elastic constant studies of $Fe_{3-x}Zn_xO_4$ ($x < 0.04$) series are reported. Adiabatic heat capacity measurements, performed on single crystals, show the clear change of the transition character from first order for low Zn content ($x < 0.012$) to the higher order in $0.012 < x < 0.035$ regime. The change of transition order is accompanied by the change in the heat capacity base lines below the Verwey transition temperature T_V. From the elastic constants measurements we found that c_{11}, $(c_{11} - c_{12})$ and c_{44} modes exhibit anomalies at T_V but only shear wave c_{44} show critical softening while approaching transition from high temperatures. This behavior can be linked to the results obtained by the heat capacity studies. These point to the important role of the lattice contribution to the mechanism of the Verwey transition.

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1. Introduction

The Verwey transition in magnetite can be described, in the simplest way, as an ordering process of the "extra" electron from Fe^{2+} (as compared to Fe^{3+}) on octahedral sites of the spinel lattice. These electrons, strongly correlated by the Coulomb repulsion and resonating between octahedral sites at high temperatures, tend to freeze out on selected octahedral positions below the Verwey temperature T_V. It is still not known what ionic pattern develops below T_V and what additional interactions are involved in the transition.

The number and the surroundings of the resonating electrons can be finely tuned by nonstoichiometry or by doping. The strongest effect on T_V is caused

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by nonstoichiometry and Zn or Ti doping [1–4]. Despite the fact that all three kinds of defects introduce different perturbations to the system the properties of $Fe_{3(1-\delta)}O_4$, $Fe_{3-x}Ti_xO_4$ and $Fe_{3-x}Zn_xO_4$ are very similar, which can be seen from the universal linear T_V vs. $3\delta = x$ dependence. Additionally, when the degree of nonstoichiometry 3δ or concentration x exceeds ≈ 0.012 the nature of the Verwey transition changes from first (I) to second (II) order; the transition disappears altogether when $3\delta = x \gtrsim 0.036$ [4].

Our studies presented below are part of the project set up to resolve the origin of the change of the transition order. Here, the results of our heat capacity studies of zinc ferrite single crystals for Zn content x falling within first and second order regime are reported. Those data are supplemented by the measurements of elastic constants in these materials.

2. Experiment

Single crystals used in our experiments were grown under a CO_2 atmosphere using the cold-crucible skull-melter technique [5]. The starting materials were 99.995% purity Fe_2O_3 and 99.9 purity ZnO. After growing the crystals were subjected to subsolidus annealing under CO/CO_2 gas mixtures to establish the appropriate metal/oxygen ratio.

Heat capacity was measured by adiabatic method in the temperature range 40–200 K [6], while for the elastic constants and attenuation studies a phase comparison and a phase sensitive (quadrature) method were used. To avoid magnetic domain effects elastic constants were measured in the external magnetic field $\mu_0 H = 0.4$–0.6 T.

3. Results and discussion

The change of transition order reflected in the shape of specific heat anomalies is accompanied by the clear change of heat capacity base line below T_V [6]. Above the transition the base lines nearly coincide, while below T_V they are split (Fig. 1). This originates from the fact that the base line for second order samples crosses the transition region continuously, but that for I order changes slope below T_V. This is particularly well seen in the inset of Fig. 1, where the characteristic Debye temperature θ_D is plotted against T; here the transition peaks were removed for clarity. To understand this phenomenon we have analyzed several possible contributions to the heat capacity and we have found, in conclusion, that most likely it results from the difference in lattice dynamics for both types of specimens below the transition [6].

Recently, neutron scattering data were published [7], that closely resemble our results. A diffuse scattering peaked at q values incommensurate with the lattice and extending far above T_V increases gradually as T_V is approached and falls sharply below the transition temperature in I order samples, but passes smoothly through the transition for II order specimens. The inelastic neutron scattering showed the existence of phonon peaks that were linked to the diffuse scattering [8]. Although no clear phonon softening was found in those studies we believe that our data give additional trigger for further search for a change in phonon spectrum.

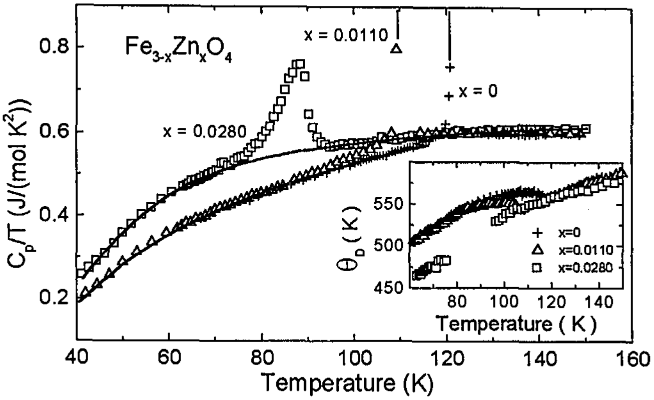

Fig. 1. Specific heat and the Debye temperature θ_D for $Fe_{3-x}Zn_xO_4$.

To show that the observed base line anomaly can be really linked to the phonon instability we have fitted the heat capacity base lines to the Einstein formula for lattice heat capacity. To keep the reasonable number of parameters we simulated the vibration spectrum by three energy levels and their densities of states. The fit of heat capacity baseline for I order samples below T_V shows that the density of states of lower energy level is diminished with the simultaneous increase in occupation of higher energy level as compared to II order specimens. In other words for I order samples the new high-energy vibration mode sets in at T_V, responsible for 50 K enhancement of θ_D temperature. The typical fits are shown in Fig. 1.

This kind of analysis is surely too simplified to show the details of the possible phonon spectrum; it shows, however, that the difference in heat capacity base lines can be accounted for the change of lattice dynamics.

The results of elastic measurements are presented in Fig. 2 where all three elastic constants c_{11}, $(c_{11}-c_{12})/2$ and c_{44} for stoichiometric magnetite are shown. The anomaly related to the Verwey transition is clearly observed for all modes (and for all samples, although the c_{11} step at T_V greatly diminishes with Zn content), but only c_{44} shows strong softening (about 10%) from room temperature down to 124 K. The normalized c_{44} for selected samples with different x are shown in Fig. 3. For the highest concentration, $x = 0.032$, a total softening of c_{44} mode amounts to 34%; here the sudden jump at $T = T_V$ observed for $x = 0$ has disappeared. Although the step in all elastic constants lowers with increasing Zn content, it is difficult to draw the firm conclusion that stoichiometric Fe_3O_4 gets more rigid at T_V, as opposed to second order Zn ferrites.

Temperature dependence of c_{44} for all samples can be well fitted by the formula $c_{44} \sim (T-T_C)/(T-\theta)$, where θ is the transition temperature in the absence of strain interactions, and T_C is the transition temperature in the free state (zero stress). This proves that strain is bilinearly coupled to the order parameter, i.e. charge fluctuation mode. The c_{44} softening is never completed (i.e. does not reach zero), which suggests that at temperatures very close to T_V other correlations develop that eventually drive the transition. This qualitatively resembles the tem-

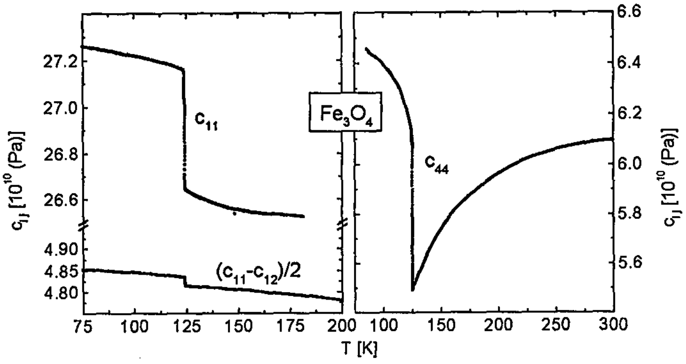

Fig. 2. Temperature dependence of the elastic constants for Fe_3O_4.

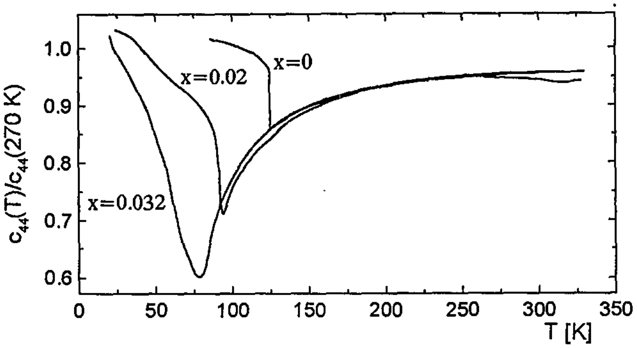

Fig. 3. Normalized c_{44} modes for $Fe_{3-x}Zn_xO_4$ series.

perature dependence of neutron diffraction pattern for Fe_3O_4 [8]. While the diffuse scattering mentioned above is visible up to 200 K, some other "spot-like" critical scattering sets forth at temperatures much closer to T_V. According to authors [8] this effect can be explained by one-dimensional correlations that grow with lowering T, finally triggering 3-dimensional ordering. Also, recent X-ray diffraction studies [9] revealed the presence of asymmetrically distributed diffuse scattering that can be related to charge ordering between Fe^{2+} and Fe^{3+} ions.

In conclusion, the difference in heat capacity data for I and II order samples are interpreted by the change of lattice dynamics at T_V for slightly doped (I order) zinc ferrites, absent in highly doped materials (II order). Elastic constant studies showed softening of c_{44} mode, suggesting that electron-lattice correlations show up already at higher temperatures.

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