

Fe₃O₄ VERWEY TRANSITION. CALORIMETRIC DETERMINATION
OF THE EFFECTS OF CONCENTRATION OF Zn AND Cd DOPANTS*

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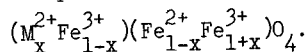
ABSTRACT

To determine the effect of increase of the lattice constant and decrease in electron concentration on the Verwey transition in Fe₃O₄, heat capacity measurements have been made on Zn- and Cd-doped Fe₃O₄ from 5 to 350 K. Bifurcation of the anomaly depends sensitively on the nature and concentration of dopant. Although high dopant levels (e.g., Cd(0.010)) occasion the diminution of the transitional enthalpy increment, for lower concentration (e.g., Cd(0.005)) the bifurcation has disappeared and both anomalies are merged into a single peak. At even higher dopant levels (e.g., Zn(0.066)) virtually no anomaly is evident over the transition region but an excess heat capacity in the region 25 to 150 K can be discerned. The doping occasions upward migration of the higher-temperature anomaly and downward migration of the lower-temperature anomaly. The former is consistent with the prediction of the Wigner crystallization model and the latter with the usual behavior of an order-disorder transition.

INTRODUCTION

The electronic transition of Fe₃O₄ at ~120 K is a well-known but poorly understood phenomenon. Previous experiments by other techniques¹ suggest that a more systematic confirmation of the mechanism of the bifurcation² of the Verwey transition of Fe₃O₄ as a Wigner-type electron crystallization was urgent especially since the expected increase in the transition temperature with the decreasing electron concentration had not been observed until recently by magnetic and electrical studies. Our recent measurements on a Mn-doped Fe₃O₄ sample revealed an upward migration in a heat-capacity anomaly associated with the Verwey transition. This finding is of sufficient

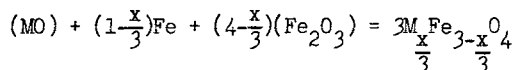
difference from previous experience and of such theoretical significance that it warranted further systematic confirmation. To this end Zn- and Cd-doped Fe₃O₄ samples have been synthesized and their thermal properties investigated especially in the region of the Verwey transition. These dopants decrease the electron concentration without disturbing the octahedral sublattice and therefore to a first approximation their effect is simply to decrease the electron concentration. They should provide good model systems for confirming whether the Verwey transitions have a marked Wigner nature. Both Zn and Cd have a clear preference for spinel tetrahedral A-sites, completely filled orbitals and have four-coordinate, Shannon and Prewitt radii of 0.50 and 0.95 Å respectively. The former value is near that Fe³⁺ (0.60 Å); therefore, at low dopant levels the zinc reduces electron concentration, as will cadmium; however, the latter will increase the unit cell size substantially. The reduction of octahedral Fe²⁺ is directly proportional to the amount of tetrahedral dopant consistent with the following formula:



We report results for M = Cd, x = 0.010, 0.005, and for M = Zn, x = 0.066, 0.005.

EXPERIMENTAL

Reactants were Johnson-Matthey Grade I "Specpure", 99.998% pure with respect to both cations and anions. Amounts of Fe₂O₃, Fe, and dopant oxide, MO, consistent with the reaction:



were dry mixed in an agate mortar, loaded into a quartz ampoule which was then evacuated to 10⁻⁶ min. and sealed off. The ampoule and contents were fired at 800 C for 8 to 14 hours, and the furnace was cooled to room temperature. After grinding and sizing (to 200 mesh or less), the sample was compressed in a steel die, the resulting pellet was loaded into a special quartz ampoule packed with alumina wool to prevent movement of the pellet, and the bottom of the ampoule was fused shut. The then evacuated and sealed ampoule and contents were fired at 985 C for 24 hours and furnace cooled. Surface layers were removed and the pellet was crushed.

X-ray powder patterns at 300 K using a Guinier-Hage camera and CuKα₁ radiation revealed a linear variation of the a₀ lattice parameter with dopant

concentration. Chemical analysis confirmed the stoichiometries within the limits of analytical accuracy.

Heat capacity measurements were made from 5 to 350 K in the Mark II adiabatic cryostat. Temperature increments as small as 50 mK were used to evaluate the details of the C_p anomalies. The entire transition region was traversed several times with single enthalpy increments to determine the total enthalpy and entropy of transition.

RESULTS

Transitional thermophysical properties of the doped-Fe₃O₄ samples including those previously published are presented in Table I. It will be observed that not only are the peaks in the heat capacity displaced by addition of the dopants in a significant manner, but that at low dopant levels the enthalpy of transition (ΔH_t) is almost independent of dopant level and this suggests that the phenomena occurring in the transition region change only slightly at low dopant levels. Moreover, it is observed that the temperature of the higher-temperature anomaly migrates upwards for low dopant levels of ions whose radii are not significantly different from those of Fe³⁺ and Fe²⁺. For larger ions, such as Cd²⁺, the effects on the thermal parameters are more dramatic. Even in the most dilute Cd sample examined Cd(0.005) the bifurcation of the anomaly is no longer present whereas in the corresponding Zn-doped sample two peaks were still observed. For higher dopant levels of either ion not only is the bifurcation no longer present but the transition itself is suppressed in size and smeared-out over a large temperature range.

Somewhat similar migration effects have also been noted for vanadium oxides⁴ and parallels exist with Ti₄O₇'s Verwey transition.⁵ This study has, however, quantified the energetics as noted in Table I. In addition, subtle changes occur in the heat capacities and entropies in regions remote from the transition especially at relatively high dopant levels. All doped samples clearly had finite heat-capacity maxima and achieved equilibria rapidly (15-20 min) without hysteresis near the maxima.

The lower-temperature transition is seen to occur at temperatures more elevated than those for pure Fe₃O₄ in several samples in table I; yet in all Cd and Zn samples and Millar's sample a significant decrease was observed. Further study will be needed at lower dopant levels to establish the initial sense and rate of change. In intermediate dopant levels e.g., Cd(0.005), the magnitude of the observed

Table I. SELECTED TRANSITIONAL PROPERTIES*

Compound	T _ℓ /K	T _h /K	ΔH _t	ΔH _ℓ	ΔH _h	ΔS _t	C _{p,ℓ} max	C _{p,h} max	Ref.
Fe ₃ O ₄	113.3	118.88	164	66	98	1.4	33.2	117	(2)
Hyd-Fe ₃ O ₄ [§]	117.0	123.0	139	68	71	1.8	27.2	(46.8)	(1)
Xtal-Fe ₃ O ₄ [¶]	117.30	(119)	140	140	--	1.2	109.6	28.8	(1)
Zn(0.005)	110.57	119.09	142	126	16	1.1	53.7	36.1	
Cd(0.005)	114.66	---	155	155	--	1.3	101.5	----	
Millar	114.2	---	108	108	--	1.0	40.	----	(3)
Cd(0.010)	105.7	---	104	104	--	0.98	31.1	----	
Zn(0.066)	80	---	70	70	--	0.87	10.4	----	

* ΔH's are enthalpy increments in cal mol⁻¹. ΔS's are entropy increments and Cp's are heat capacities; both in Cal K⁻¹ mol⁻¹. Subscripts on thermodynamic quantities--t, ℓ, and h--refer to total lower temperature, and higher temperature transitions.

[§]Corresponds to Mn(0.008)

[¶]Two large magnetite crystals.

ΔH_t and the single transition imply the coincidence of both transitions. At still higher concentrations further suppression, downward migration, and smearing-out of the transitions are found.

DISCUSSION

This study confirms the reality of the bifurcation originally observed in synthetic Fe₃O₄² on samples prepared in different laboratories, by different techniques beyond any reasonably doubt. The profiles and the ΔH_t's of the two anomalies permit us to draw tentative conclusions about the mechanism underlying the transitions. For example the upward migration of the high-temperature anomaly at low-dopant levels for decreases in electron concentration is consistent with its description as an essentially pure electron crystallization of the Wigner-type. The relative insensitivity of the low-temperature peak to impurities as well as its gradual suppression with increased impurity levels and its downward migration is consistent with ascription to a phenomenon of the more usual order-disorder type with a second order character and its relation to a structural transition. Similar systematics occur in VO₂ and Ti₄O₇.^{4,5}

Bifurcation is seen to be affected both by identity and quantity of dopant. The results of this study indicate that most other measurements on Fe₃O₄ have been made on relatively impure materials. The effects of impurities have been mistakenly attributed as being those of a pure sample. Millar's³ impurity level, for example, must approximate that of Cd(0.005) since both show a single anomaly. In addition, the much greater influence of Cd²⁺ doping on the thermal anomalies relative to that of Zn²⁺ is consistent with these systematics inasmuch as Cd causes a greater lattice expansion than does Zn at an equivalent dopant concentration. At higher levels it is no longer correct to treat the dopant as a minor perturbation on the lattice system because of the real differences in the parameters of the ions concerned. The model thus becomes inapplicable and at sufficiently high dopant levels the distortions predicted by molecular-field approximations become relevant.

Samara⁶ observed a decrease in the transition temperature of Fe₃O₄ with increasing pressure. The observed increase in the temperature of the higher-temperature transition at low dopant levels observed in this study is entirely consistent with the results of Samara if one describes the transition as a Wigner crystallization. These data are also totally consistent with the observations of Miyahara,⁷ who found consistent decreases in the magnetization transition temperature of Al, Co, Ni, Cu, Zn, and Ti dopants at concentrations greater than 0.05.

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- * Supported by the National Science Foundation.
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