

Heat capacity of $\text{Fe}_{3-\alpha}\text{M}_\alpha\text{O}_4$ ($\text{M}=\text{Zn}, \text{Ti}$, $0 \leq \alpha \leq 0.04$)

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Systematic studies of the specific-heat anomaly and of the entropy changes at the Verwey transition in the $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ and $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$ series are reported. These investigations clearly demonstrate that in $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ and $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$, as in magnetite, there occurs only one, well defined phase transition. In the composition range $0 \leq x, y < 0.012$ the phase transition is of first order, as manifested by extremely sharp spikes in the specific-heat curve at the transition temperature T_v ; for $0.012 < x, y < 0.04$ the transition is of second or higher order, consistent with the broadened specific-heat anomalies near T_v . Deviations from the undoped Fe_3O_4 state result in a lowering of the transition temperature and in a concomitant diminution of the entropy of the transition in a manner very similar to nonstoichiometric magnetite. The difference in heat capacity below T_v for the first- and second-order samples is analyzed and the lattice properties are identified as the principal factor responsible for this difference. [S0163-1829(96)01741-9]

INTRODUCTION

The Verwey transition in magnetite has been extensively studied since 1926; heat-capacity (C_p) measurements represent a basic aspect of these investigations. Past work has been characterized by a wide diversity of findings; careful adjustment of oxygen stoichiometry has lately been shown¹⁻³ to be absolutely essential for obtaining reproducible results. A summary of earlier heat-capacity work can be found in Ref. 1; additional investigations since 1983 are listed in Refs. 2-6. It has been demonstrated^{1,6} that for $0.0005 < \delta < 0.0039 \equiv \delta_c$ in $\text{Fe}_{3(1-\delta)}\text{O}_4$ the Verwey transition is of first (I) order; the transition temperature T_v diminishes linearly with increasing cation vacancy density. For $\delta_c < \delta < 3\delta_c$ the transition is of second or higher order (II), with a further diminution in T_v as δ is increased. For $\delta \approx 3\delta_c$ one reaches the magnetite-hematite phase boundary.

These findings were confirmed by electrical transport studies and by Mössbauer measurements^{7,8} on $\text{Fe}_{3(1-\delta)}\text{O}_4$ (O series). It has also been shown that titanomagnetites, $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ (T series) and zinc ferrites, $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$ (Z series), exhibit almost identical electrical transport properties,^{9,10} with the correspondence $3\delta \Leftrightarrow x \Leftrightarrow y$. Discontinuities in transport coefficients at T_v were encountered in the range $0 < x, y < 3\delta_c$ and discontinuities in their slope (with variations in temperature T) at T_v were observed for $3\delta_c < x, y < 9\delta_c$. The advantage of Ti and Zn doping over oxygen excess is the accessibility of the regime $x = y > 9\delta_c$, for which no Verwey transition was noted in the electrical

studies. It therefore appeared to be of interest to complement the above transport studies with a systematic determination of the heat capacities of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ and $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$, which is basic to a thermodynamic characterization of the Verwey transition in magnetite.

Several experimental findings from previous C_p results on O compounds have already been cited; among the most important are:

(1) The entropy of the transition for stoichiometric magnetite is close to $\Delta S_v = R \ln 2$ per mole and decreases with increasing degrees of nonstoichiometry δ .⁶ The variation of S_v with δ was mimicked by the phenomenological model formulated by Aragón and Honig,¹¹ based on the approach pioneered by Strässler and Kittel (SK).¹² The interacting electron system was parametrized by a quasi-two-level model with degeneracies g_0 and g_1 which, when fitted to experimental results for T_v vs nonstoichiometry, led to $g_1/g_0 = 2$ and 1 for first- and second-order samples, respectively. This model was further extended by Honig and Spalek in Ref. 13, where the SK model was derived as a limiting case of a microscopic order-disorder model. The system is simulated by pairs of octahedrally coordinated Fe ions in the Fe^{+2} and Fe^{+3} valence state, giving rise to three energy levels of the system, with interactions simulated by the energy separation between the levels which varies with the degree of their occupation. With rising T successive states are gradually occupied, with a sudden change of occupancy at T_v , which results in a sharp increase of entropy ΔS_v close to T_v .¹⁴ The data collected so far led to ΔS_v

values for first order very close to those theoretically predicted. Such an analysis was not performed for the second-order samples, because of large errors arising from problems of baseline determinations (see below).

(2) Heat capacities for I- and II-order samples are very nearly equal above their transition temperatures, but C_p for I-order samples is much lower than that of II-order samples below their transition temperature. This vital point provides experimental support for the hypothesis that highly nonstoichiometric samples really undergo a second- or higher-order transition (and not a series of closely spaced first-order transitions at the Verwey point, as suggested by some theories¹⁵); this is a starting point for the discussion of the lattice contribution to the differences in heat capacities below T_v . Both of the above-mentioned experimental facts should be checked out for the T and Z series as well. The results of our investigations are described below.

EXPERIMENTAL DETAILS

The T and Z samples were grown in single-crystal form using the cold crucible, skull melting technique¹⁶ which avoids contamination by crucible material. Particular care was taken to ensure attainment of the ideal 4/3 oxygen to cation stoichiometry ratio, by appropriate CO/CO₂ anneals.¹⁷⁻¹⁹ The titanium and zinc content and uniformity of distribution were monitored by electron microprobe techniques.

To check the reproducibility of our results two distinct sets of measurements were undertaken: a relaxation-type calorimeter of the type described in Ref. 20 was employed at Purdue University, whereas an adiabatic calorimeter of standard design, described at length in Ref. 21, was used at Kraków. Apiezon N grease served as a thermal contact for bonding the samples to the sapphire plate which also contained an evaporated heating element. A calibrated Pt thermometer was used in the adiabatic calorimeter down to the cryogenic temperature range, below which an RuO₂ thermometer was employed; the estimated error in temperature measurements was ± 0.3 K. In the relaxation arrangement an unencapsulated GaAsP diode was employed. Data acquisition occurred under computer control. Careful examination of the data sets showed excellent agreement between the measurements carried out on the two types of equipment with respect to the C_p

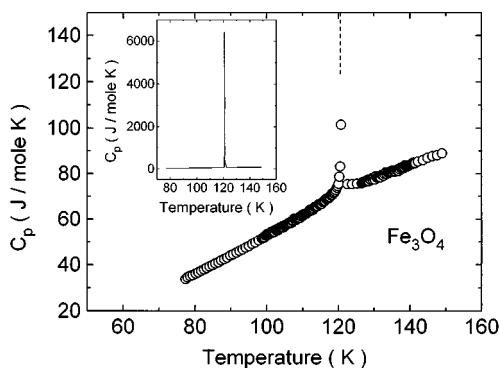


FIG. 1. Heat-capacity measurements of stoichiometric Fe₃O₄ showing the sharp Verwey transition at 121 K.

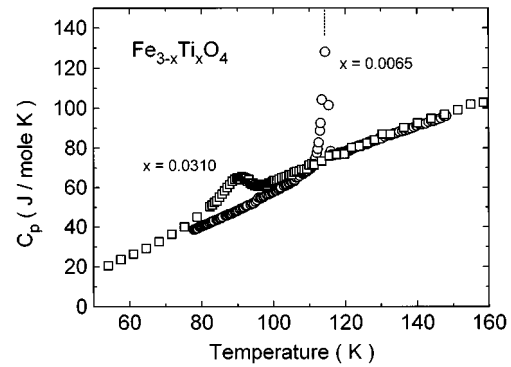


FIG. 2. Typical heat-capacity data for Fe_{3-x}Ti_xO₄ in the first- ($x=0.0065$) and second-order ($x=0.0310$) transition regimes.

anomalies, and the values of the Verwey transition temperature T_v .

EXPERIMENTAL RESULTS

Typical heat-capacity (C_p) vs temperature (T) curves are displayed in Figs. 1, 2, and 4. Figure 1 shows measurements on pure Fe₃O₄, in excellent agreement with earlier work.^{1,6} One should note the very sharp peak in C_p at $T_v=121$ K, as well as the small pre- and postmonitory effects in the baseline. Figure 2 displays results for Fe_{3-x}Ti_xO₄ with $x=0.0065$ in the first-order and with $x=0.0310$ in the second- (or higher) order regime; the corresponding ‘‘raw’’ effective Debye temperature $\theta(T)$ (calculated from the total heat-capacity data) is shown in Fig. 3. In Fig. 4 are shown typical heat-capacity data for Fe_{3-y}Zn_yO₄ for $y=0.0110$, subject to the first-order-type transition, and for $y=0.0280$, corresponding to the second-order regime. The Debye θ vs temperature relation for these compounds is shown in Fig. 5. These results are typical of a large number of investigations on the Z and T systems. In Fig. 6 we plot T_v vs 3δ , x , and y for nonstoichiometric magnetite, dilute titanomagnetites, and zinc ferrites; the composite includes the earlier C_p and electrical-transport measurements on Fe_{3(1- δ)O₄.^{1,6,7} The heat-capacity anomalies for the first-order transitions are broader in the T and Z series than for Fe_{3(1- δ)O₄. This presumably reflects the difficulty in achieving uniform Ti and}}

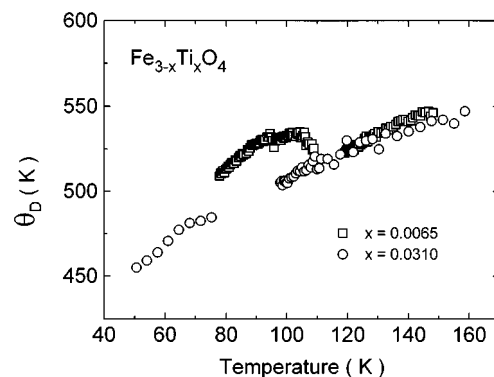


FIG. 3. Variation of the effective Debye temperature θ with T for first- and second-order transition regime of Ti-doped magnetite samples.

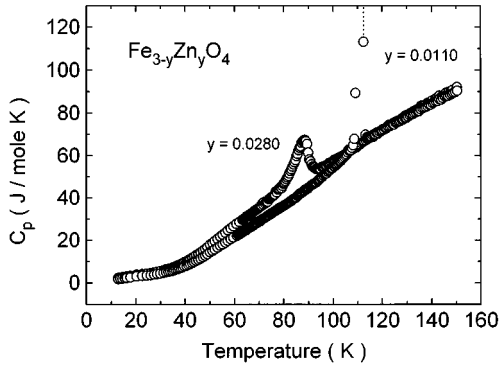


FIG. 4. Typical heat-capacity data for $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$ in the first-order ($y=0.0110$) and second-order ($y=0.0280$) transition regime.

Zn distributions, as compared to the more uniform cation vacancy density, because of the much lower diffusion rate for the former as compared to the latter species. Nevertheless, the Verwey temperature could always be clearly identified from the peak position of the C_p vs T curve.

In Table I we present the entropies ΔS_v of the Verwey transition calculated from our data compared with the data from the literature; only heat-capacity measurements exhibiting a single peak were included. The large spread in ΔS_v values shows very clearly the difficulty in estimating entropies by taking the areas under the heat-capacity anomalies because of the uncertainties in drawing the appropriate baseline.

DISCUSSION

The following points are noteworthy:

(1) There is a close analogy between C_p measurements for the O , T , and Z series. This is not surprising, because at the dilute concentrations under study the properties of the host lattice dominate. However, the heat-capacity data for Ti samples lie slightly above those of other compounds. The reason for this minor discrepancy is unclear.

(2) Figure 6 shows that the $3\delta \leftrightarrow x \leftrightarrow y$ correspondence applies to thermodynamic properties as well as to electron-transport characteristics, for which this correspondence had been established earlier.^{9,10} Also, one can clearly recognize the first-order and second-order regimes on this composite

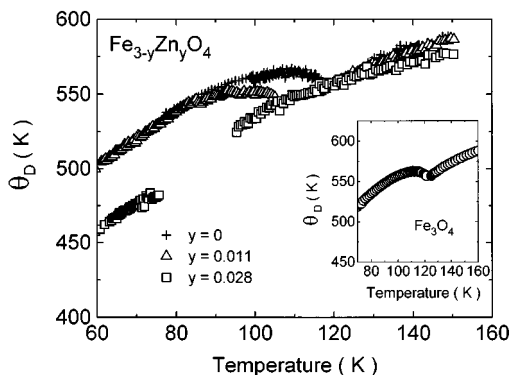


FIG. 5. Variation of the effective Debye temperature θ with T for selected samples of Zn-doped magnetite. Inset shows $\theta(T)$ curve after Takai *et al.* (Ref. 28).

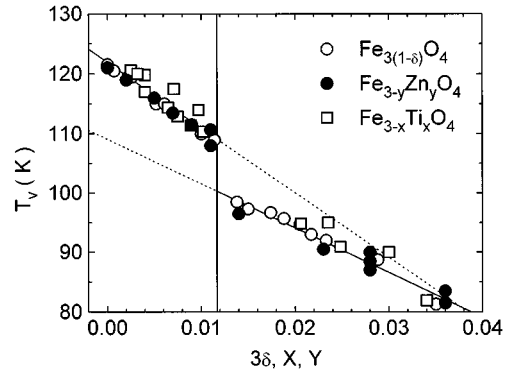


FIG. 6. Composite plot of Verwey transition temperature vs ferrite composition in the O , T , and Z series. Data based on C_p , and electrical resistivity measurements. For $0 < 3\delta, x, y < 3\delta_c$ one encounters first-order transitions in the range 121–110 K. For $3\delta_c < 3\delta, x, y < 9\delta_c$ one encounters second-order transitions in the range 100–81 K.

plot. As already mentioned, a rationalization of these results has been furnished;^{13,14} in particular, the ratio of the slopes of the straight lines, $\ln 2$, can be interpreted on the basis of order-disorder theory^{11,26} of first- and second-order transitions. All these suggest that the Verwey transition should be linked to the ratio of divalent to trivalent iron occupying the octahedral interstices. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be altered either by incorporating excess oxygen on anion sites or by doping with Zn^{2+} or Ti^{4+} which exclusively enter the tetrahedrally or octahedrally coordinated cation interstices, respectively.

(3) Above T_v the baselines of all samples merge, while below T_v those of the second-order specimens in the T or Z series are higher than those of the first order, as is clearly seen in Figs. 2 and 4.

(4) There is a sudden shift of $\theta(T)$ at $T \approx T_v$ for first-order samples (Figs. 3 and 5) in comparison to the $\theta(T)$ extrapolated from high T ; no such shift exists for second-order samples.

Those last two experimental observations are naturally interconnected; our further discussion is mainly devoted to these facts.

The common heat-capacity baselines for temperatures above the transition for all three series and both orders can be rationalized by the fact that the specific heat at this region is dominated by the lattice component, which should be almost the same for all samples under consideration: all samples have cubic symmetry above T_v and the differences in lattice dynamics caused by dopants and/or vacancies are too small to be noticeable. Also, we did not observe any short-range order or fluctuation effects in the specific-heat curves at $T \geq 10$ K above the transition. Other contributions (e.g., magnetic excitation contribution) are also too small to be detected.

For temperatures below T_v contributions to the specific heat aside from the lattice component may be considered. The first contribution relates to magnon excitations. This problem has been treated in several papers on $\text{Fe}_{3(1-\delta)}\text{O}_4$, e.g., Ref. 5, where the magnon component for first- and second-order transition samples have been estimated from low-temperature C_p data ($0.3 < T < 10$ K), assuming the con-

TABLE I. Summary of the data pertaining to the Verwey transition. and the entropy of transition. c indicates fractional vacancy concentration.

T_v (K)	ΔS_v (J/mole K)	Sample description	Reference
115.0	5.44	Fe ₃ O ₄ , natural crystal	22
114.2	4.39	Fe ₃ O ₄ , natural crystal	23
80.0	3.46	Fe ₃ O ₄ , 0.66 at. % Zn, natural crystal	24, 25
114.7	5.44	0.5 at. % Cd, natural crystal	24, 25
105.7	4.11	Fe ₃ O ₄ , 1.0 at. % Cd, natural crystal	24, 25
123.6	6.24	Fe ₃ O ₄ , $c < 5 \times 10^{-6}$, single crystal	2
116.6	5.44	Fe ₃ O ₄ , $c = 1.5 \times 10^{-2}$, single crystal	2
122.8	5.40	Fe ₃ O ₄ , $c = 10^{-5}$, powdered crystal	2
121.6	4.73	Fe ₃ O ₄ , $c = 4 \times 10^{-4}$, polycrystalline Fe ₃ O ₄ ,	2
118.4	4.14	$c = 2 \times 10^{-3}$, polycrystalline	2
123.8	6.16	Fe ₃ O ₄ , single crystal	28
120.8	5.98	Fe ₃ O ₄ , single crystal	1
120.4	5.80	Fe _{3(1-δ)O₄} , $\delta = 0.0002$, single crystal	1
119.4	5.60	Fe _{3(1-δ)O₄} , $\delta = 0.0007$, single crystal	1
114.9	5.30	Fe _{3(1-δ)O₄} , $\delta = 0.0017$, single crystal	1
109.7	4.00	Fe _{3(1-δ)O₄} , $\delta = 0.0035$, single crystal	1
97.5	1.73	Fe _{3(1-δ)O₄} , $\delta = 0.0049$, single crystal	1
95.0	1.63	Fe _{3(1-δ)O₄} , $\delta = 0.0068$, single crystal	1
89.0	1.78	Fe _{3(1-δ)O₄} , $\delta = 0.0096$, single crystal	1
81.5	1.08	Fe _{3(1-δ)O₄} , $\delta = 0.0121$, single crystal	1
121.0	5.80	Fe ₃ O ₄ , single crystal ^a	This work
120.6	5.90	Fe _{3-x} Ti _x O ₄ , $x = 0.0025$, single crystal ^b	
120.0	5.20	Fe _{3-x} Ti _x O ₄ , $x = 0.0032$, single crystal ^b	
119.8	5.90	Fe _{3-x} Ti _x O ₄ , $x = 0.0040$, single crystal ^a	
114.4	4.80	Fe _{3-x} Ti _x O ₄ , $x = 0.0065$, single crystal ^a	
117.5	4.10	Fe _{3-x} Ti _x O ₄ , $x = 0.0071$, single crystal ^b	
112.9	4.80	Fe _{3-x} Ti _x O ₄ , $x = 0.0075$, single crystal ^a	
114.0	3.50	Fe _{3-x} Ti _x O ₄ , $x = 0.0097$, single crystal ^b	
95.0	1.20	Fe _{3-x} Ti _x O ₄ , $x = 0.0235$, single crystal ^b	
90.0		Fe _{3-x} Ti _x O ₄ , $x = 0.0310$, single crystal ^b	
119.0	5.30	Fe _{3-y} Zn _y O ₄ , $y = 0.0020$, single crystal ^b	
116.0	3.30	Fe _{3-y} Zn _y O ₄ , $y = 0.0050$, single crystal ^b	
110.7	4.20	Fe _{3-y} Zn _y O ₄ , $y = 0.0110$, single crystal ^a	
90.0	0.70	Fe _{3-y} Zn _y O ₄ , $y = 0.0280$, single crystal ^b	
88.5	2.00	Fe _{3-y} Zn _y O ₄ , $y = 0.0280$, single crystal ^a	
83.5	0.75	Fe _{3-y} Zn _y O ₄ , $y = 0.0360$, single crystal ^a	

^aAdiabatic technique.

^bRelaxation technique.

ventional $C_p \sim T^{3/2}$ relation. In our case this contribution is three orders of magnitude smaller than the experimentally determined specific heat and can be neglected.

A second contribution, for second-order transitions, relates to the thermal fluctuations ultimately leading to the Verwey transition, giving rise to an additional specific-heat component not far from the transition. The fluctuation component should be absent for first-order samples.

A third possible contribution arises from the above-mentioned order-disorder models: the energy separation between ground and excited states is smaller for II- than for I-order samples at all $T < T_v$ (see Fig. 10 of Ref. 6). This means that excited energy states are more populated for II-order samples, thus leading to $C_p^{\text{II}} > C_p^{\text{I}}$, as is experimentally observed at $T < T_v$.

The last two contributions might explain the difference in heat capacities between I- and II-order samples mentioned in point (3) above. However, this explanation seems to contradict the θ vs T behavior depicted in Figs. 3 and 5. We would expect a smoothly varying ‘‘raw’’ $\theta(T)$ for first-order samples (additional components are small), whereas for the second-order materials, due to possible additional contributions beyond the lattice component, $\theta(T)$ should decrease as T falls below the transition temperature. What we observe is just the reverse: there is a shift of $\theta(T)$ at $T \approx T_v$ for first-order samples in comparison to the $\theta(T)$ extrapolated from high T , which shows that the specific heat below T_v cannot be obtained by a simple extrapolation of its high T ($T > T_v$) dependence. In contrast, for second-order specimens $\theta(T)$ is a smoothly varying function across the transition. These ob-

servations imply that contributions other than lattice components are absent, or are too small to be detected; we thus suggest that the observed jump in θ is mainly due to a change in lattice dynamics.

If we adopt the above conclusions the picture emerges that the lattice of the first-order samples rapidly becomes more rigid as T falls below T_v . This is in agreement with the observed sharp increase of sound velocity in Fe_3O_4 when the sample is cooled down through the transition.²⁷ No such sudden change of structure is present for second-order samples. The Debye temperature for these two structures differ by about 40–50 K, roughly comparable to the values 539 and 511 K for I and II order $\text{Fe}_{3(1-\delta)}\text{O}_4$ samples, cited by Koenitzer⁵ from measurements in the low-temperature region. The similar shift in θ for stoichiometric magnetite was also observed by Takai *et al.*²⁸ (see the inset of Fig. 5); however, no conclusions were drawn by them with respect to second-order samples.

It is well established that the structure of stoichiometric magnetite changes at the transition from cubic above T_v to presumably monoclinic²⁹ (or triclinic³⁰) below this temperature. There are no available high precision data concerning the crystal structure of $\text{Fe}_{3(1-\delta)}\text{O}_4$, $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$, and $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ($x, y < 0.04$) below T_v , but both the Verwey transition and a sudden change of the easy axis of magnetization observed in these materials could be interpreted as an indication of the same change of structure as in magnetite. However, it was reported recently,^{31,32} that long-range crystalline order is actually missing below T_v for second-order samples: instead, the system was reported to break into small domains (approximately 28 cubic unit cells for $\delta = 0.006$) diminishing in size with rising nonstoichiometry.³² The vibration spectrum of such a collection of domains may be much softer than that of the uniform structure and may resemble the vibration spectrum of the cubic lattice. Our data stress the need for a precise structure determination of nonstoichiometric and/or slightly doped magnetite. Such measurements are now in progress.³³

Whatever the reason for the break of $\theta(T)$ near 120 K for first-order samples, the fact that no common base line below and above T_v exists must be taken into consideration when calculating the total entropy of the transition. This entropy may involve the component due to the lattice symmetry change. The proposed evaluation of this component is based on the premise that in the temperature region 85–117 K (see Fig. 7) the heat capacity for samples of both orders is dominated by pure lattice contributions (for I order: low- T lattice, for II order, high- T lattice). Then, the entropy that must be released by the low- T structure so that its heat capacity eventually coincides with the high- T result is at least as large as the area shown in Fig. 7 (inset), i.e., is equal to ~ 1.9 J/mole K. This may be regarded a lower bound on the estimate of the lattice component of the entropy. The tentative assumption that it is principally the lattice specific heat which contributes to C_p below T_v for II-order samples, and allows us to integrate the area between C_p/T vs T of I- and II-order samples to arrive at an upper bound for the lattice component in the transition as 2.7 J/mole K. These remarks suggest that the lattice introduces a significant component to the entropy of Verwey transition.

If we assume that the dynamics of first- and second-order

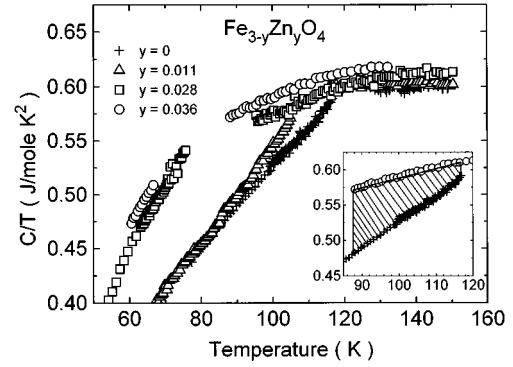


FIG. 7. C_p/T vs temperature for selected $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$ samples (transition peaks are removed), showing clearly the difference in C_p between first- and second-order transition regime below T_v . Calculation of the minimum difference in lattice entropies between a sample with $y = 0.036$ and stoichiometric magnetite is suggested in the inset (coordinates are the same as on the main figure).

lattices is the same above the transition (based on the same specific heat for these T), one may calculate the total entropy change from 0 K. The difference in the entropy for first- and second-order samples then becomes a measure of the number of electronic states involved in the Verwey transition. The data for the total entropy of stoichiometric magnetite and the one with $\delta = 0.0121$ (second-order regime) shows (Fig. 8 of Ref. 6) that these values are the same to within 2%. If correct, it suggests that the number of electronic energy levels involved in the Verwey transition is the same, irrespective of the order of transition.

In summary, we have presented heat-capacity measurements on $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ and $\text{Fe}_{3-y}\text{Zn}_y\text{O}_4$ which complement earlier studies on $\text{Fe}_{3(1-\delta)}\text{O}_4$. As for magnetite we encounter a single first-order-type transformation in the range $0 < x, y < 3\delta_c = 0.0117$, and a broad anomaly, extending over a large temperature interval, in the range $3\delta_c < x, y < 9\delta_c = 0.035$. The Verwey transition temperature T_v decreases linearly with increasing x and y , in two distinct regimes corresponding to the first and second (or higher) order-type transition. The difference in heat capacity below T_v for first- and second-order samples was analyzed and is correlated with the difference in lattice properties between these classes of materials: there is a change of elastic properties in first-order samples, while no such change is present in second-order specimens. This suggests that the lattice contribution to the Verwey transition should be considered. Such an interplay between structural and electronic transitions was observed in the A-15 superconducting materials³⁴ and discussed in high- T_c superconductors.³⁵ Nevertheless, precise neutron-scattering and/or elastic properties measurements are required to complement our heat-capacity data and to cross-check our suggestions.

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