

## Heat capacity of magnetite in the range 0.3 to 10 K

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Heat-capacity measurements are reported for  $\text{Fe}_{3(1-\delta)}\text{O}_4$  samples with  $\delta=0$  and 0.0049 in the range 0.3 to 10 K. Differences in the heat-capacity curves are discussed. The Debye temperatures are 539 and 511 K, respectively; the corresponding exchange integrals as evaluated from Kouvel's model are  $J_{AB}=2.35$  and 0.604 meV, respectively.

### INTRODUCTION

We report briefly on the heat capacity ( $C_p$ ) of magnetite crystals in the temperature range 0.3–10 K. These studies extend earlier<sup>1</sup> and concurrent specific-heat measurements in our laboratory to still lower temperatures. The investigations were initiated to check on the possibility of the existence of a soft lattice mode that might be detected at low temperatures. Furthermore, there are wide variations in reported values of both the Debye temperatures and the magnetic exchange constant of magnetite.<sup>2</sup> Our experience with several different physical measurements on  $\text{Fe}_{3(1-\delta)}\text{O}_4$  (Refs. 1 and 3) have demonstrated the crucial importance of properly controlling the nonstoichiometry,  $\delta$ , of these specimens. It appears likely that discrepancies in earlier measurements by other investigators are due to inadequate precautions regarding the preparation of appropriate samples. Special care was therefore taken by us in the preparation of high-quality material.

### EXPERIMENTAL TECHNIQUES

Single crystals were grown by the skull melting technique described elsewhere in detail,<sup>4</sup> starting with iron oxides of 99.999% purity. Samples were subjected to subsolidus annealing under an appropriate oxygen fugacity to achieve values of  $\delta=0$  and  $\delta=0.0049$  in  $\text{Fe}_{3(1-\delta)}\text{O}_4$ ; the relevant procedures have been described

elsewhere.<sup>3(b)</sup> The exterior portions of the sample were then removed to eliminate inhomogeneities introduced during the quenching process. Heat capacity measurements were carried out in a <sup>3</sup>He adiabatic calorimeter; a full description of the experimental apparatus is available.<sup>5</sup> The magnetite samples were attached to a sapphire sample holder by GE No. 7031 varnish diluted in ethanol.

The accuracy of the calorimeter is estimated to be within  $\pm 3\%$ ; the major source of error arises from the temperature calibration. The sample masses and relative sample contribution to the total observed heat capacity are entered in Table I.

### RESULTS AND DISCUSSION

Heat-capacity data for magnetite of nearly-ideal stoichiometry ( $\delta \approx 0$ ) and for an off-stoichiometric sample ( $\delta=0.0049$ ) are displayed in Fig. 1. There is no evidence for any soft-mode behavior in these measurements which extend to lower temperatures than earlier studies reported in the literature.<sup>1,6–10</sup>

The remaining discussion must be understood in the context of recent findings<sup>1(a)</sup> that in the range  $-0.0005 < \delta < 0.0039 = \delta_C$  (regime I) the Verwey transition in  $\text{Fe}_{3(1-\delta)}\text{O}_4$  is first order, whereas in the range  $0.0039 \leq \delta < 0.012$  (regime II) the transition is of second or higher order. This feature is readily demonstrated by the presence or absence of a latent heat effect when samples in the two composition regimes undergo the transformation.<sup>1(a)</sup>

The above dichotomy is also reflected in the heat-capacity data taken in the range  $0.3 < T < 10$  K, as displayed in Fig. 1. The  $C_p$  data for the sample with  $\delta=0.0049$  [curve (b)] clearly lie above the corresponding data for a sample of essentially ideal stoichiometry,  $\delta \approx 0$  [curve (a)]. At the highest temperatures of the present experiments these two curves approach from below the  $C_p$  data reported earlier for these samples<sup>1</sup> in the range  $5 \text{ K} < T < T_V$ , where  $T_V$  is the Verwey transition temper-

TABLE I. Sample mass and sample heat capacity as percent of the total heat capacity of different temperatures.

$T$ (K)	$\text{Fe}_{3(1-\delta)}\text{O}_4$	$\text{Fe}_{3(1-\delta)}\text{O}_4$
	$\delta=0.0000$	$\delta=0.0049$
	$m=6.5317$ g	$m=1.6469$ g
1	88%	90%
5	80%	72%
9	75%	65%

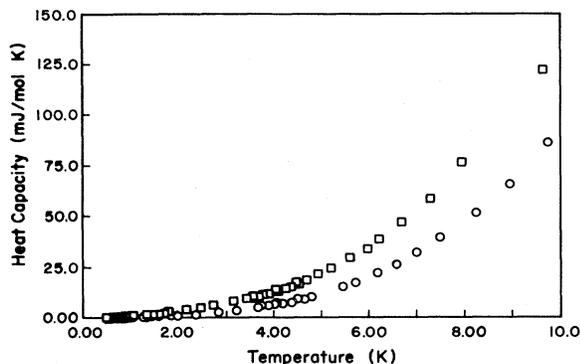


FIG. 1. Heat capacity of  $\text{Fe}_{3(1-\delta)}\text{O}_4$  in the cryogenic temperature range.  $\circ$ ,  $\delta=0$ , first-order regime;  $\square$ ,  $\delta=0.0049$ , second-order regime. The size of the symbols indicate the approximate experimental errors.

ature. Below  $T_V$  all samples of regime II have higher heat capacities than are displayed by specimens belonging to regime I. By contrast, above their respective Verwey transition temperatures, and within experimental error, all  $C_p$  versus  $T$  curves are virtually identical. These facts make it unlikely that measurements for specimens with  $\delta > \delta_C$  are simply smeared-out first-order Verwey transitions. Rather, there appear to be a genuine difference in lattice characteristics of  $\text{Fe}_{3(1-\delta)}\text{O}_4$  with  $\delta < \delta_C$  as compared to  $\delta > \delta_C$ . One would expect such differences to be reflected in the parameters characterizing the heat capacity data.

The present data sets were analyzed in terms of a model invoking spin wave and phonon excitations. This model has quite generally been used by workers in the field to interpret the low-temperature heat capacity data of ferrites. As a zero-order approximation to the treatment by Kouvel<sup>6</sup> one finds that the heat capacity should depend on temperature according to

$$C = LT^{3/2} + \alpha T^3. \quad (1)$$

The first term in the above expression deals with spin excitation effects; here

$$L \simeq 0.113R [2(2S_B - S_A)k / 11J_{AB}S_A S_B]^{3/2} \quad (2)$$

with average spin quantum numbers  $S_B = \frac{9}{4}$ ,  $S_A = \frac{5}{2}$ ;  $R$  is the gas constant, and  $J_{AB}$  is the dominant magnetic exchange integral for nearest-neighbor iron ions located in the tetrahedral ( $A$ ) and octahedral ( $B$ ) cation sites. In the second term which deals with lattice contribution,  $\alpha \simeq 1944n / \Theta_D^3$  J/mole  $\text{K}^4$ , where  $n$  is the number of atoms in the elementary unit cell, and  $\Theta_D$  is the Debye temperature.

A test for the applicability of Eq. (1) is provided by plots of  $C_p/T^{3/2}$  versus  $T^{3/2}$  which should yield a straight line. Such plots are shown in Fig. 2; in each case a reasonably good straight-line fit is encountered. Data taken in the range 0.3 to 7 K were used to evaluate the slopes, which yielded a least-squares fit of  $\Theta_D^I = 539 \pm 47$  K and  $\Theta_D^{II} = 511 \pm 24$  K for the Debye temperatures of

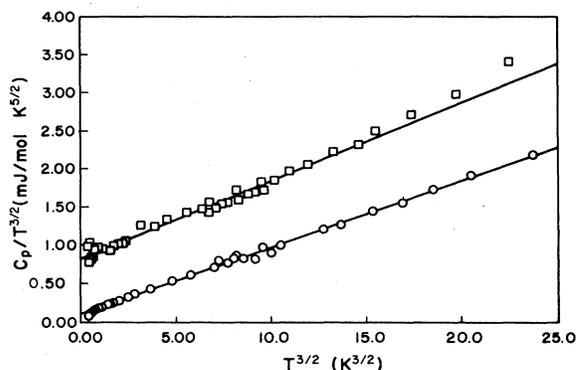


FIG. 2. Plot of  $C_p/T^{3/2}$  vs  $T^{3/2}$  for  $\text{Fe}_{3(1-\delta)}\text{O}_4$ .  $\circ$ ,  $\delta=0$ , first-order regime;  $\square$ ,  $\delta=0.0049$ , second-order regime. The size of the symbols indicates the approximate experimental errors.

group-I and group-II specimens, respectively. The corresponding exchange integrals, as determined by the intercepts are  $J_{AB}^I = 2.35 \pm 0.25$  meV and  $J_{AB}^{II} = 0.604 \pm 0.11$  meV.

The above Debye temperatures compare with values in the range of 480 to 660 K cited in the literature.<sup>2,6-9</sup> In an earlier investigation for a somewhat higher temperature range Gmelin *et al.*<sup>10</sup> reported a decrease of  $\Theta$  from 560 to 480 K when nearly stoichiometric magnetite was rendered highly cation deficient; the trend is quite similar to that described above.

The magnetic exchange interaction energies reported here require a much smaller degree of data extrapolation than do the earlier results<sup>2,6-9</sup> and thus permit a more precise estimate to be made of the exchange energies. The quantity  $J_{AB}^I = 2.35$  meV is in almost perfect agreement with values determined by neutron scattering experiments, reviewed in Ref. 2, or with values calculated<sup>10</sup> from magnetization and magnetic susceptibility data, or from magnon scattering experiments.<sup>11</sup> One must, however, keep in mind that Eq. (2) involves many simplifying approximations, including the dubious assumption that other types of magnetic exchange integrals are small relative to  $J_{AB}^I$ . All earlier estimates of  $J_{AB}$  via heat capacity measurements fell considerably below the quantities determined from Fig. 2.

The very small value of  $J_{AB}^{II}$  indicates the changes in magnetic excitations that can be brought about by alterations in the compositional homogeneity attendant to non-stoichiometry. This is a reasonable result since cation vacancies disrupt magnetic exchange effects. The present results also explain the wide spread in  $J_{AB}$  values reported in the literature. A detailed microscopic interpretation of these effects must await structural studies which are in progress.

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