Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

Mol. Cryst. Liq. Cryst. 1984, Vol. 107, pp. 191-194
0026-8941/84/1072-0191/$18.50/0

HEAT CAPACITY STUDIES ON MAGNETITE

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Abstract Single crystals of magnetite were grown and annealed under a controlled oxygen atmosphere to produce homogeneous, single phase samples. Heat capacity studies revealed a single, sharp first order heat capacity transition at the Verwey transition, no anomaly at 10 K, and an entropy of transition of $\Delta S = R \ln 2$ per mole of Fe_3O_4.

INTRODUCTION

The Verwey electrical transition in Fe_3O_4 has been investigated numerous times ever since the original report on this phenomenon by Verwey and coworkers[1]. As is by now well established, this transformation occurs over a small temperature interval (0.1-0.9K) in the neighborhood of $T_V = 120$ K; the precise value of T_V depends on the oxygen stoichiometry[1,2]. Despite intense theoretical analysis over a period of several decades, the microscopic origin of the electrical transition is not well understood; it seems to be closely linked to charge ordering, but the precise nature of the ionic configuration is still in doubt[3].

In conjunction with the electrical measurements the thermodynamic characteristics of the Verwey transition have repeatedly been investigated by heat capacity measurements[4]. In contrast to the sharp resistivity change at the Verwey temperature the heat capacity anomaly reported by all investigators so far extended over some 10 K; in several instances a double peak was encountered.

Careful scrutiny of the reported experimental techniques suggest that control over sample stoichiometry may have been inadequate and that more careful sample handling could perhaps narrow the temperature range of the heat capacity anomaly near the Verwey transition temperature. A preliminary report of our recent findings is provided below.

EXPERIMENTAL TECHNIQUE

Samples of magnetite were grown in a skull melter whose operation is discussed elsewhere in detail[5]; an appropriate CO/CO_2 mixture was used to maintain the requisite partial pressure of oxygen. After cooling, a small section of a single crystal was reannealed under an appropriate CO/CO_2 atmosphere whose partial oxygen pressure was monitored with a solid state electrochemical cell[6]. After quenching, a 40 mg specimen was cut, polished, and mounted on a relaxation calorimeter designed by Griffing and Shivashankar [7].

Results of a typical run are shown in Fig. 1. In addition, the calorimeter was operated in a transition mode so as to obtain cooling and heating curves in the vicinity of the Verwey temperature. From these data the entropy of transition could be computed.

RESULTS

As is obvious from Fig. 1, the conditions used for the synthesis of the Fe_3O_4 specimens were such as to alter dramatically the nature as well as the temperature range of the transition; the anomaly extends over a range of less than 0.3 K and consists of a single first order heat capacity peak with a tail no more than 2 - 3 K in width. The baseline continues smoothly from $T < T_V$ to $T > T_V$, suggesting the absence of significant short range ordering above the transition. There is no heat capacity anomaly close to 10 K, of the type which had been encountered in earlier work[8].

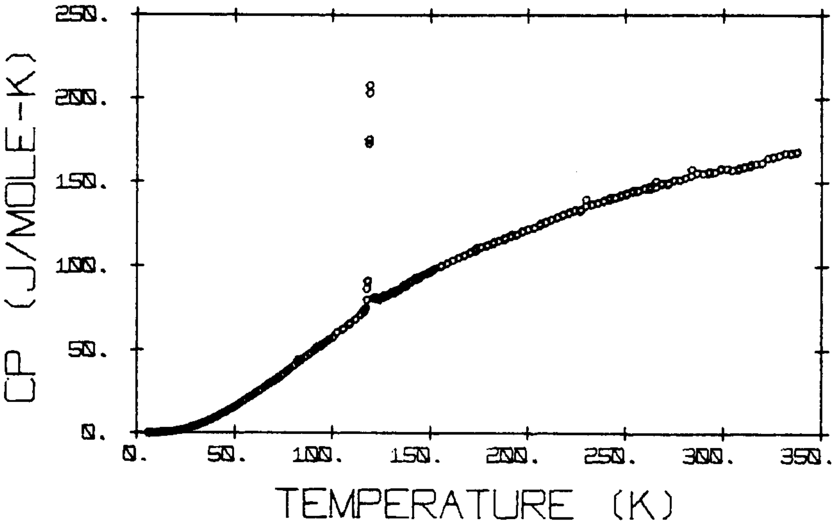

FIGURE 1. Specific heat per mole of Fe_3O_4, magnetite.

From the heating and cooling curves, the entropy change was calculated to be very close to the theoretical value of $\Delta S = R \ln 2$ per mole of Fe_3O_4.

The above findings are quite different from those encountered in prior heat capacity measurements. If confirmed by further measurements, these new results would put severe constraints on any model purporting to deal with the Verwey transition. In addition, the investigation shows how sensitive the thermodynamic measurements are to non-uniformities in sample composition.

Further work is in progress; the results will be reported elsewhere in detail.

ACKNOWLEDGMENT

This research was supported on grant DMR-81-03041 A02 by the National Science Foundation. The skull melter unit was acquired on a NSF grant DMR-79-11137.

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