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Heat Capacity and Metal-Insulator Transitions in Ti_4O_7 Single Crystals

C. Schlenker, S. Lakkis, and J. M. D. Coey
Groupe des Transitions de Phases, Centre National de la Recherche Scientifique, 38 042 Grenoble-Cedex, France

and

M. Marezio
Laboratoire des Rayons X, Centre National de la Recherche Scientifique, 38 042 Grenoble-Cedex, France
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Heat-capacity and entropy changes at the metal-insulator transitions have been measured on Ti_4O_7 single crystals. The 130-K transition is related to a disordering of the Ti^{3+} and Ti^{4+} chains at the unit cell level. Ti^{3+} pairing occurs in this phase but without any long-range order of the bonds. It is shown from both magnetic-susceptibility and specific-heat data that for the 150-K transition, the electronic contribution seems to be of the same order of magnitude as the lattice contribution.

Titanium oxide Ti_4O_7 belongs to the class of materials which show metal-insulator transitions and have attracted considerable attention during the last decade.[1,2] It is one of the Magnéli phases Ti_nO_{2n-1} and is triclinic with two molecules per primitive cell.[3] The structure contains two types of Ti chains, running parallel to the pseudorutile c axis and truncated every four Ti by the crystallographic shear planes.[4] Ti_4O_7 exhibits two electrical transitions, a semiconductor-semiconductor transition at about 130 K and a semiconductor-metal one at about 150 K.[5] For both transitions, there is a steep increase of the electrical conductivity with increasing temperatures. The magnetic susceptibility shows a sharp enhancement at 150 K; it is small and temperature independent both below and above 150 K and does not show any anomaly at 130 K.[6] Marezio *et al.* showed that, below 130 K, the Ti chains are either Ti^{3+} or Ti^{4+} and that the 3+ sites are paired to form nonmagnetic Ti^{3+}-Ti^{3+} bonds [Figs. 3(a) and 3(b)]. Between 130 and 150 K, the crystal structure was found to be only slightly different from the room-temperature one.[4]

It was proposed that the low-temperature phase ($T < 130$ K) is insulating because of the localization of $3d$ electrons into nonmagnetic Ti^{3+}-Ti^{3+} bonds. The high-temperature phase ($T > 150$ K) is metallic because of the delocalization of the $3d$ electrons. The nature of the intermediate phase ($130 < T < 150$ K) is not clear. It has been suggested that there could be charge localization

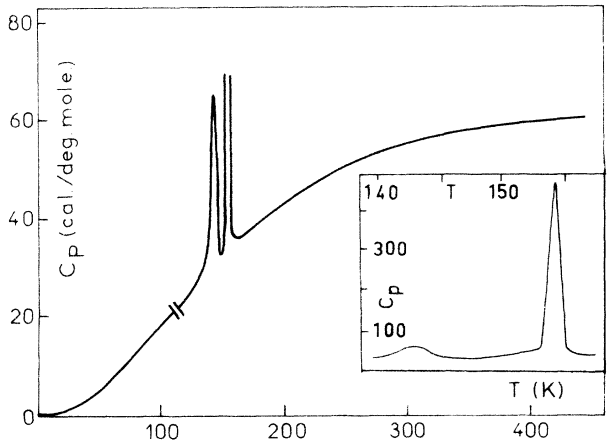

FIG. 1. Molar heat capacity C_p of Ti_4O_7. Measurements are made at low temperature on powder (2 g) and above 110 K on single crystals of 25×10^{-3} g. The inset shows the molar heat capacity of single crystals in the temperature range of the transitions. The measurements are performed with increasing temperatures.

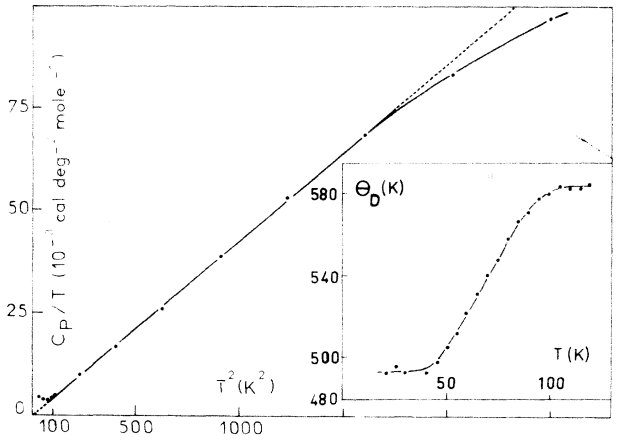

FIG. 2. C_p/T versus T^2 for $T<50$ K. The corresponding Debye temperature is 493 K ± 10 K. The inset shows the Debye temperature Θ versus T and the strong deviation from the Debye theory above 40 K.

and Ti^{3+} pairing also in the intermediate phase, but without any long-range order. Recently, Anderson discussed such a phase as a "classical liquid of pair bonds."[7]

Until now no experimental evidence for the validity of such a model has been given. In this Letter, the first heat-capacity data obtained on Ti_4O_7 single crystals are presented. The single crystals were grown by chemical transport reaction as described elsewhere.[8] X-ray and electron-diffraction studies showed that the crystals were single phased. The data obtained for the electrical resistivity and the magnetic susceptibility are very similar to those given in Refs. 5 and 6.

The heat capacity at constant pressure, C_p, has been measured in the temperature range of 100 to 400 K for several crystals, with a Perkin-Elmer DSC2 differential-scanning calorimeter. The errors on C_p are of the order of 2%. The curve of C_p versus T (Fig. 1) shows two peaks: The high-temperature peak is centered at 154 K and is 3 K wide; the low-temperature peak is about 10 K wide and is centered at 142 K for increasing temperatures and at 130 K for decreasing temperatures. Measurements have also been performed on powder samples at lower temperatures with a differential calorimeter.[9] The enthalpies of the transitions are found to be 95 ± 5 and 468 ± 5 cal/mole for the 130- and 150-K transitions, respectively. The corresponding entropy changes are 0.70 ± 0.05 and 3.40 ± 0.05 cal/mole deg.

In order to fit the data with the Debye theory, the $C_p - C_v$ correction has been calculated at room temperature, with the volume thermal expansion coefficient and the molar volume deduced from data of Marezio *et al.*[10] for Ti_4O_7 and the tabulated compressibility of TiO_2. This correction is found to be negligible at 300 K. In the high-temperature phase, the heat capacity approaches the C_v equipartition value of 66 cal/mole deg. At low temperature, the $C_p - C_v$ correction, being much smaller than at room temperature, is also negligible. Figure 2 shows the curve of C_p/T versus T^2 obtained from the low-temperature measurements on powder samples. Between 10 and 40 K, C_p follows a T^3 law corresponding to a Debye temperature of 493 K ± 10 K. Above 40 K, the results deviate from the Debye theory, and the Debye temperature Θ (as deduced from tabulated values) increases with temperature (Fig. 2, inset).

The departure from the T^3 law below 10 K might be due to some impurities. The Debye temperature of 493 K obtained between 10 and 40 K is smaller than the values of 674 and 760 obtained for Ti_2O_3[11] and TiO_2,[12] respectively. The same kind of result has been obtained for V_4O_7 compared to VO_2 and V_2O_3[13] and might be characteristic of the crystal structure of the Magnéli phases. The deviation from the Debye theory

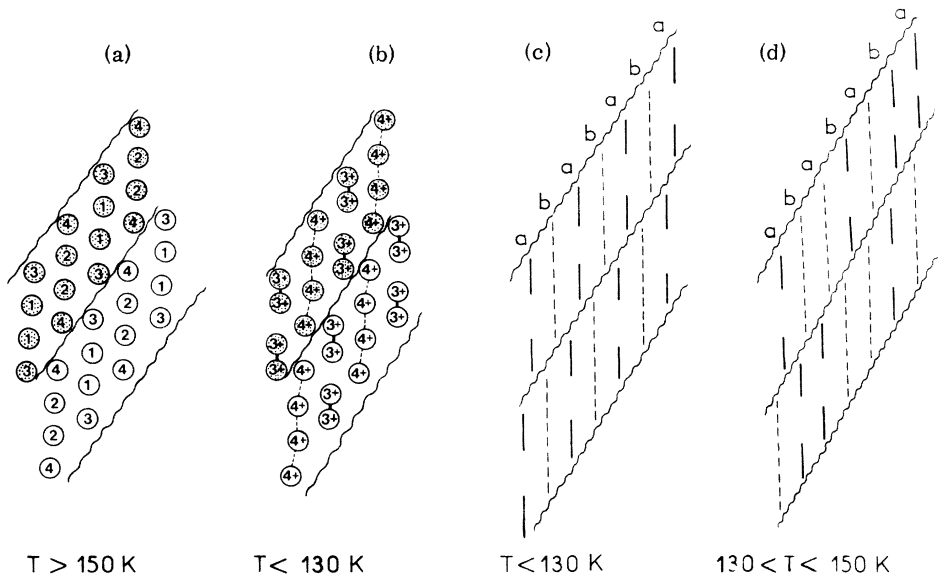

FIG. 3. Crystal structure showing only the Ti chains parallel to the pseudorutile c axis and truncated every four Ti by a shear plane. (a) Structure in the metallic phase. (b),(c) Structure of the phase stable below 130 K. (d) Proposed structure with disordered Ti^{3+}-Ti^{3+} bonds for the intermediate phase. The a(3-1-1-3) chains contain the Ti(1) and Ti(3) sites, while the b(4-2-2-4) chains contain the Ti(2) and Ti(4) sites.

above 40 K indicates that the phonon frequency spectrum $g(\omega)$ does not follow the Debye quadratic law even for rather small ω.

The measured molar entropy change $\Delta S = 0.70$ cal/mole deg at the 130-K transition corresponds approximately to two configurations per primitive cell. This result suggests the model of disordered Ti^{3+} and Ti^{4+} chains shown in Fig. 3(d). If we call the 3-1-1-3 chain a and the 4-2-2-4 chain b, the two pairs of Ti^{3+} ions may be located either on chain a or on chain b, and similarly for the Ti^{4+} ions; no more than two consecutive chains can be occupied by ions of similar charge. An exact calculation for this model yields a value for the partition function of 2.62^N for N cells, if the same statistical weights are given to the configurations $Ti^{3+}(c)$-$Ti^{4+}(c)$-$Ti^{3+}(c)$-$Ti^{4+}(c)$, $Ti^{3+}(c)$-$Ti^{4+}(c)$-$Ti^{4+}(c)$-$Ti^{3+}(c)$, etc., where $Ti^{3+}(c)$ and $Ti^{4+}(c)$ mean Ti^{3+} chain and Ti^{4+} chain. This calculation is not physically correct. In fact, if a statistical weight of 1 is given to the configuration $Ti^{3+}(c)$-$Ti^{4+}(c)$-$Ti^{3+}(c)$-$Ti^{4+}(c)$ stable below 130 K, then the configurations including two consecutive chains occupied by the same ions [such as $Ti^{3+}(c)$-$Ti^{4+}(c)$-$Ti^{4+}(c)$-$Ti^{3+}(c)$] must have a statistical weight a less than 1. The configurations including twice two consecutive chains occupied by the same ions [such as $Ti^{3+}(c)$-$Ti^{3+}(c)$-$Ti^{4+}(c)$-$Ti^{4+}(c)$] will have a statistical weight $b \sim a^2$. The number of configurations per unit cell is then smaller than 2.62. The experimental data correspond to a value of 0.7 for a, indicating an extra energy of approximately 3 meV for the configuration $Ti^{3+}(c)$-$Ti^{4+}(c)$-$Ti^{4+}(c)$-$Ti^{3+}(c)$ compared to the $Ti^{3+}(c)$-$Ti^{4+}(c)$-$Ti^{3+}(c)$-$Ti^{4+}(c)$. The kind of disorder suggested in this model is compatible with the x-ray data,[4] where the thermal parameters of the Ti ions in the intermediate phase are reported to be anomalously large.

The low value for the susceptibility in both the intermediate- and low-temperature phases can be explained by the fact that the $3d$ electrons are paired in the Ti^{3+}-Ti^{3+} bonds. The temperature-independent behavior might be due to a Van Vleck mechanism, as was proposed for titanium sesquioxide Ti_2O_3.[14] The steep increase of the susceptibility at 150 K can be attributed to a delocalization of the electrons and therefore to a Pauli contribution. If one takes for the Pauli contribution $\Delta\chi \simeq 600 \times 10^{-6}$ emu/mole, one obtains an effective mass $m^* \simeq 15m$ and a density of states at the Fermi level of 10 eV^{-1} per $3d$ electron. The heat-capacity peak at 150 K includes an electronic contribution which can be roughly evaluated from the susceptibility results. The effective

mass of $15m$ leads to a γ coefficient of approximately 0.01 cal/mole deg^2 and to an electronic entropy change of 1.50 cal/mole deg. The γ value is much larger than for usual metals and is of the same order of magnitude as the values found in V-doped Ti_2O_3,[11] Ti-doped V_2O_3,[15] and other vanadium oxides.[13] This result might be characteristic of a highly correlated electron gas for the metallic phase.[13] For the 150-K transition, as the total entropy change is 3.40 cal/mole deg, the electronic contribution to the transition seems to be of the same order of magnitude as the lattice contribution. Therefore, the electron-phonon interactions are likely to play an important part in the 150-K transition, although the electron correlations in the $3d$ band of the metallic phase are not taken into account in this interpretation. Further work is in progress and will be published later.

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Temperature-Dependent Spin-Disorder Resistivity in a Van Vleck Paramagnet

N. Hessel Andersen, P. E. Gregers-Hansen, E. Holm, and H. Smith
Physics Laboratory I, H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

and

O. Vogt
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, Zürich, Switzerland
(Received 21 March 1974)

We have measured the resistivity of single-crystal paramagnetic $Tb_xY_{1-x}Sb$ with $x=0$, 0.05, 0.20, 0.40. At low temperatures a resistance anomaly develops in proportion to x. The observed resistance anomaly reflects the temperature-dependent probability that the conduction electrons are scattered from the crystal-field–split $4f$ levels of the Tb ions by elastic as well as inelastic processes. A calculation of this anomaly yields excellent agreement for those values of x for which indirect exchange can be neglected.

In the last few years there has been an increasing interest in the crystal-field splitting of the $4f$ electronic level of the rare earth ions and its many profound effects.[1] If the ion is of the non-Kramers type (J integral), the crystal-field–only ground state may be a singlet. In such a