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# Heat Capacity and Metal-Insulator Transitions in $Ti_4O_7$ Single Crystals

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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

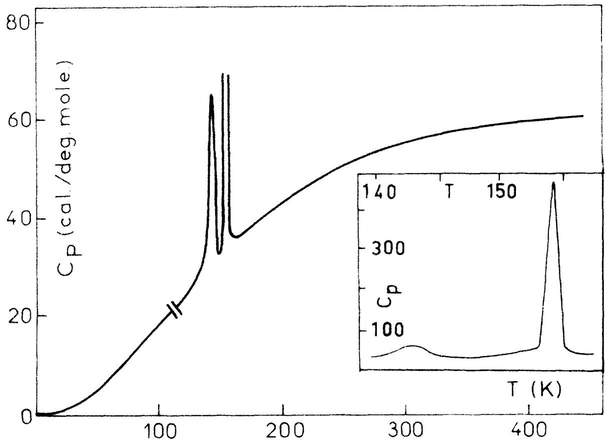


FIG. 1. Molar heat capacity $C_p$ of $Ti_4O_7$. Measurements are made at low temperature on powder (2 g) and above 110 K on single crystals of $25\times10^{-3}$ g. The inset shows the molar heat capacity of single crystals in the temperature range of the transitions. The measurements are performed with increasing temperatures.

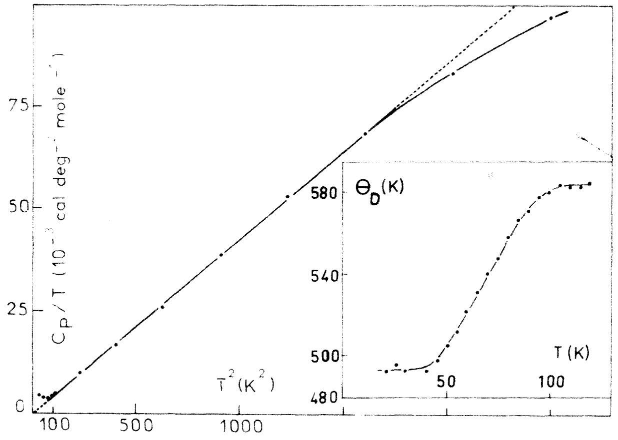


FIG. 2. $C_p/T$ versus $T^2$ for $T < 50$ K. The corresponding Debye temperature is 493 K ± 10 K. The inset shows the Debye temperature Θ versus $T$ and the strong deviation from the Debye theory above 40 K.

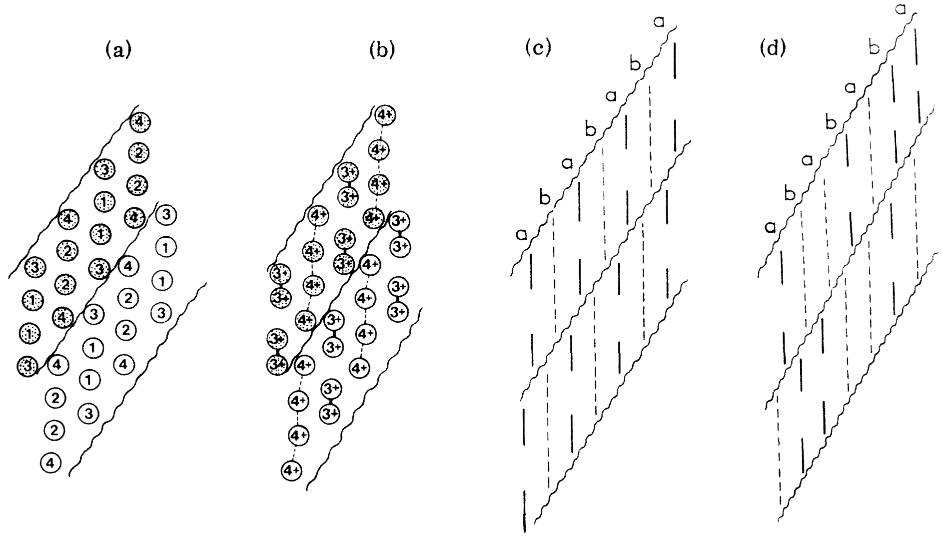
and $Ti^{3+}$ pairing also in the intermediate phase, but without any long-range order. Recently, Anderson discussed such a phase as a "classical liquid of pair bonds."[7]

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



T > 150 K T< 130 K T<130 K 130<T< 150 K

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 $\omega$.

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 3*d* 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$_2$O$_3$.[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 3*d* 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 $\gamma$ coefficient of approximately 0.01 cal/mole deg$^2$ and to an electronic entropy change of 1.50 cal/mole deg. The $\gamma$ value is much larger than for usual metals and is of the same order of magnitude as the values found in V-doped $\mathrm{Ti_2O_3}$,[11] Ti-doped $\mathrm{V_2O_3}$,[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

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We have measured the resistivity of single-crystal paramagnetic $\mathrm{Tb}_x\mathrm{Y}_{1-x}\mathrm{Sb}$ 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