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N.F. Mott. Metal-insulator transition in Ti_2O_3 . Journal de Physique, 1981, 42 (2), pp.277-281.
10.1051/jphys:01981004202027700 . jpa-00209009

HAL Id: jpa-00209009

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Classification
Physics Abstracts
72.20D

Metal-insulator transition in Ti_2O_3

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(Reçu le 22 juillet 1980, accepté le 8 octobre 1980)

Résumé. — On décrit la transition métal-isolant dans Ti_2O_3 comme une transition où les bandes se chevauchent. Il y a formation d'un gaz électrons-trous lorsque l'énergie libre devient plus grande que la bande interdite.

Abstract. — The metal-insulator transition in Ti_2O_3 is described as a bandcrossing transition, an electron-hole gas forming when its free energy becomes greater than the gap.

Ti_2O_3 , which has the corundum structure, is at low temperatures a semiconductor, the optical band gap being 0.2 eV (Lucovsky, Allen and Allen [1]). At about 400 K there is a transition [2] to a *metallic* state with conductivity in the range 10^3 - $10^4 \Omega^{-1} \cdot \text{cm}^{-1}$, accompanied by an increase in the ratio c/a , and the disappearance of the optical gap [1]. This occurs in a range of T of order 100° ; the transition is not of first order even for the purest specimens. The material is normally non-stoichiometric and conduction at low temperatures is either extrinsic or within an impurity band. Admixture with V_2O_3 introduces moments, spin-glass behaviour and impurity conduction, both variable-range hopping and metallic behaviour being observed as the vanadium content is increased (Dumas and Schlenker [3]). Chandrashekar *et al.* [4], however, showed that the transition at 400 K persists up to 10% vanadium, the temperature being little changed.

In addition to much experimental work, many attempts at a theoretical description have been made, for instance that of Zeiger [5] and of the present author [6]; it is supposed that both the valence and conduction bands come from the 3d titanium orbitals, of a_{1g} and e_g^π symmetry, whose edges approach and cross with increasing temperature. X-ray analysis confirms that the electrons occupy a_{1g} sites [7]. This assumption will be made here. The present author has supposed that the overlap at high temperature was small, while earlier work from the Purdue group [5] came to the opposite conclusion; however a recent investigation by Chen and Sladek [8] on piezoresistivity lead them to the conclusion that the overlap is much smaller than they had previously assumed.

The purpose of this paper is to present a new explanation of the origin of the transition. A hypothesis made by the present author in previous work

was that the change in c/a with increasing T or V content is linked with a decrease in the gap; the entropy of electrons excited across the gap would then increase with n , the number excited. Thus as T increases, minimizing the free energy will decrease the gap, which will eventually disappear. But this hypothesis is ruled out by the behaviour of the alloy system $(\text{Ti}_{1-x}\text{V}_x)_2\text{O}_3$. There is a change in c/a with increase of x , as in pure Ti_2O_3 with increase of T , the ratio reaching the values for *metallic* Ti_2O_3 when $x \simeq 0.1$. As shown by Dumas and Schlenker [3], however, in this material the vanadium, at any rate for small concentrations, is in the state $3d^3$, and to ensure charge neutrality defects are formed at which a *hole* is localized, giving a Ti^{4+} ion. These as already stated give rise to a p-type impurity band, leading first to variable range hopping ($\sigma = A \exp(-B/T^{1/4})$) and then with increasing x to metallic conduction. For concentrations for which $x \leq 0.1$, however, an increase in conductivity at $T \sim 400$ K is still observed (Chandrashekar *et al.* [4]), and as Goodenough (priv. comm.) pointed out some years ago, this shows that, while *holes* either in the valence band or impurity band will change c/a , this change does not have a major effect on the gap. This conclusion is confirmed by optical measurements due to Lucovsky [9] and by band calculations by Ashkenazi and Chuchem [10]. In $(\text{Ti}_{1-x}\text{V}_x)_2\text{O}_3$ for $x > 0.1$, we think that the impurity band has merged so strongly with the valence band that the transition at 400 K no longer occurs, or that it has disappeared for some other reason to be discussed below.

This note examines the origin, then, of the transition at 400 K, in the pure material. The standard treatment of metal-insulator transitions in systems where an indirect gap does decrease towards zero, as a consequence for instance of alloying, is as fol-

lows. The treatment is due to Brinkman and Rice [11]. Making use of the concepts developed to describe electron-hole droplets, they write for the energy of a gas of electrons and holes with density n of each per unit volume, the sum of kinetic and potential energies,

$$2(\hbar^2/m^*) n^{2/3} - A(e^2/\kappa) n^{1/3}. \quad (1)$$

Here m^* is the reduced mass $m_1 m_2/(m_1 + m_2)$, κ the background dielectric constant and A a numerical constant depending on the forms of the bands, correlation, etc. (1) has a minimum when

$$n^{1/3} = \frac{1}{4} A/a_H, \quad a_H = \hbar^2 \kappa/m^* e^2 \quad (2)$$

and the energy is then $-E_0$ where

$$E_0 = \frac{1}{8} A e^2/\kappa a_H. \quad (3)$$

When, due to pressure or change of composition, the gap ΔE becomes equal to E_0 , a discontinuous change in n from zero to a value given by (2) is expected.

If free energy F is plotted against the parameter x of which the variation changes ΔE , for instance the composition of an alloy, a curve such as that of figure 1 is expected, leading at $T = 0$ to a two-phase region between A and B. As the temperature rises, the present author supposes that the *kink* disappears and that above a critical temperature the two-phase region disappears too. No quantitative discussion has been given of this process, but it must be supposed that electron-hole minidroplets, of whatever size gives the lowest free energy, are excited in large numbers.

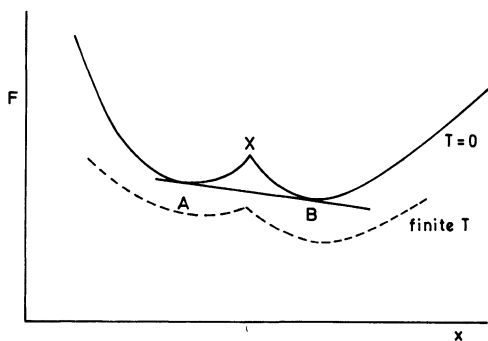


Fig. 1. — Free energy as a function of composition at a metal-insulator transition.

In Ti_2O_3 , we suppose that the gap ΔE is slightly greater than that required for the transition to occur. For a finite value of T , however, the second term in (1) should be replaced by the free energy. As we shall see below, in Ti_2O_3 the electrons are much heavier than the holes; we suppose that the electron gas is therefore non-degenerate. Moreover, we suppose that the electrons are heavy enough to be located on individual sites, so that the entropy of n such electrons distributed among N sites is

$$S = k C_n^N = k \ln \{ N!/(N-n)! n! \}.$$

This assumption is not essential; formulae for a non-degenerate or nearly non-degenerate gas could be used. With this assumption the free energy of n electrons in the conduction band is

$$(2 \hbar^2/m^*) n^{5/3} - A(e^2/\kappa) n^{4/3} + n \Delta E_F - TS \quad (4)$$

and this has a minimum when

$$\frac{10}{3} \frac{\hbar^2}{m^*} n^{2/3} - \frac{4}{3} A(e^2/\kappa) n^{1/3} + \Delta E_F - 3kT \ln \{ (N/n)^{1/3} \} = 0. \quad (5)$$

Here ΔE_F is the energy difference between the Fermi energy and the bottom of the conduction band. We plot the left hand side of (5) against $n^{1/3}$ in figure 2. The zero at A gives the number excited into the band, giving a value differing little from

$$n/N = \exp(-\Delta E_F/kT).$$

The zero at B corresponds to a maximum in the free energy, and that at C to a minimum. Thus when the curve crosses the horizontal axis at C a metal-insulator transition will occur.

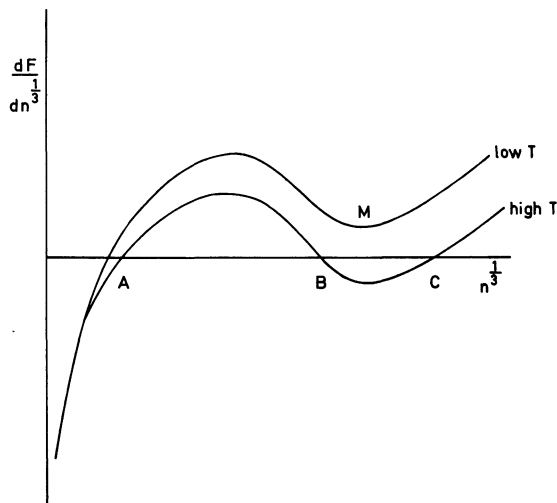


Fig. 2. — Derivative of free energy as explained in the text.

The theory as presented will give a discontinuous first order transition of n from a small value to a much larger one at a given value of T , and thereafter a slow increase in n . But we think that below the predicted temperature, our *minidroplets* will be excited, giving perhaps a plot of n against T as in figure 3, with a vertical slope at T_c , which is the point where the minimum M in figure 2 first touches the horizontal axis. The transition should then be of second order.

Two sets of observations suggest that this is the case; the first is that of Chen and Sladek [8] on the piezoresistivity already referred to, and some of whose results are shown in figure 4. Figure 5 (Sladek, priv. comm.) shows the resistivity for the same specimen. It will be seen that the kink does indeed

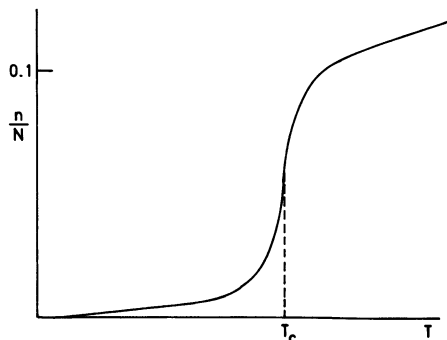


Fig. 3. — Number n of excited electrons (schematic).

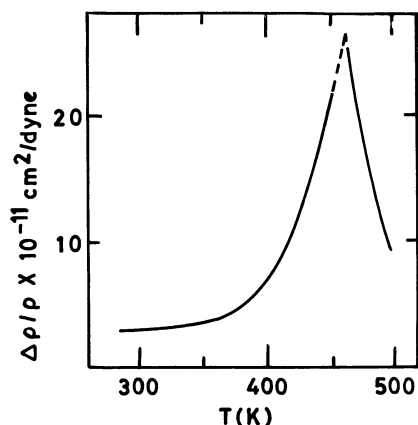


Fig. 4. — Piezoresistivity of Ti_2O_3 for uniaxial compression parallel to the c axis.

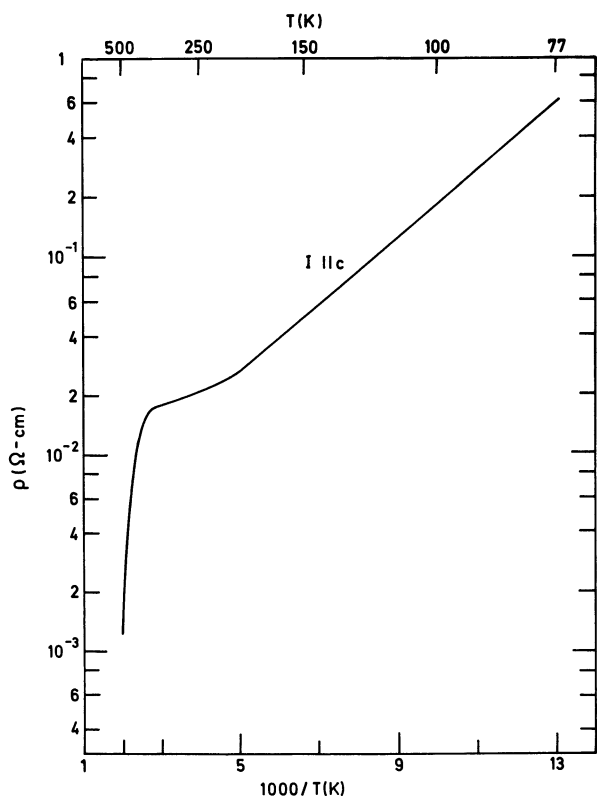


Fig. 5. — Resistivity ρ for specimen of figure 4.

appear roughly where the rate of change of the resistivity is greatest. A high or perhaps vertical slope is thus expected in figure 3 at the temperature where d^2n/dT^2 changes sign.

The second piece of evidence is the kink [12] in the plot of specific heat against temperature T , shown on figure 6. The entropy corresponds to about $n/N \sim 0.1$, if the electron gas is non-degenerate.

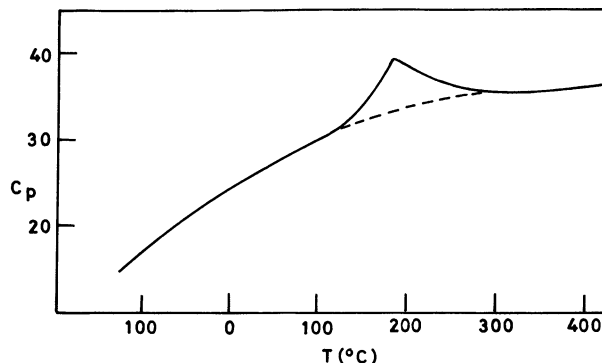


Fig. 6. — Specific heat in cal./mole C_p of Ti_2O_3 .

We now discuss the electronic behaviour somewhat further. The material is p-type, and as we have already assumed, it is likely that the electrons are heavier than the holes and that the entropy in the metallic phase comes mainly from the former, the holes at any rate forming a degenerate gas. There is, I believe, no firm evidence that the electrons make any observable contribution to the conductivity ⁽¹⁾.

Calculations by Ashkenazi and Chuchens [10] give for electrons in the conduction band $m = 6 m_e$; later calculations (Ashkenazi, priv. comm.) give an even greater difference. Earlier work by Yahia and Frederikse [13] gave $5.5 m_e$ for the electrons. These results are for a rigid band. Following a suggestion [6] made by the present author in 1969, it is possible that the electrons (not the holes) form small dielectric polarons, which have the effect of considerably enhancing the effective mass say to $30 m_e$ or more. This assumption has the following advantages :

(a) The specific heat at the transition could be accounted for if about 10% of the electrons in the valence band (Ti^{3+}) were excited into the conduction band giving a non-degenerate gas. A mass of about $30 m_e$ is necessary to give non-degeneracy, and thus the required entropy.

(b) We need not suppose that the rigid bands actually overlap in the *metallic* phase, but only that the intrinsic gap has dropped below the energy W_p of the polaron, which might be ~ 0.1 eV. The model,

⁽¹⁾ Goodenough [14] has remarked that the magnetoresistance of Ti_2O_3 varies quadratically with magnetic field at 4.2 K and that this is not compatible with a one-band model. It is however compatible with conduction in an impurity band, either hopping or metallic, if it is due to contraction of the orbits by the field.

then, differs from that of Barros *et al.* [15] in which above 400 K the overlap between bands becomes considerable, Ti_2O_3 becoming a normal metal with degenerate bands.

(c) Since in a dielectric polaron the energy W_p is gained by displacing the neighbours of the ion on which the electron sits, if the number of electrons in the conduction band rises about 0.1, each one will compete for the same ion and W_p will become small. In the author's earlier paper it was suggested that this was why, once in the metallic phase, c/a does not go on increasing with an increase in the number of carriers and the accompanying specific heat. This then, might account for the fact that the specific heat bump dies out at 600 K.

A criticism of the polaron model (Chen and Sladek [8]) is that, if

$$W_{\text{polaron}} = \frac{1}{2} \frac{e^2}{r_0} \left\{ \frac{1}{\kappa_\infty} - \frac{1}{\kappa} \right\}$$

the large value of κ_∞ for a small band-gap material would not be compatible with an appreciable polaron energy. The transition across the gap is however probably forbidden, and we are not sure how important this criticism is. Moreover Lucovsky, Sladek and Allen [16] find $\kappa_\infty \simeq 29$ from the optical behaviour. If we take κ to be ~ 45 and $r_0 = 2 \text{ \AA}$ this would give $W_p = 0.042$; mass enhancement is still not negligible and if (Austin and Mott [17])

$$m_{\text{polaron}} \simeq 5 m_e \exp(W_p / \frac{1}{2} \hbar \omega)$$

a considerable mass enhancement is possible if the bare mass is large enough for small polaron formation.

The polaron hypothesis, then, seems not unreasonable but is not essential for our model if m_e is large enough.

Some of the entropy driving the transition may be due to a soft phonon mode. Chandrashekhar *et al.* [4], however, quoting Raman results of Raccah and Moradian [18], which shows that the phonon a_g mode is shifted downward in frequency, say that the small magnitude of the softening seems to eliminate the possibility that the transition is mainly phonon-driven.

We turn next to the paramagnetic susceptibility; the results quoted from various authors (Dumas [17]) are shown in figure 7. To explain such a result, we have to assume there is some increase of n with T above the region where the C_v anomaly disappears,

as is indeed predicted by our model. This increases not only the number of magnetic carriers (non-degenerate electrons) but also the Fermi surface area for the holes. We could then make use of a hypothesis put forward by Massenet *et al.* [20] in their discussion of $\text{BaV}_x\text{Ti}_{1-x}\text{S}_3$, another material in which a broad band overlaps a narrow one. These authors suppose that the heavy electron polarizes the degenerate gas of holes, giving a moment that increases as the Fermi surface area of the holes increases. This could well happen here. However no other experiments have been made at so high a temperature, and other explanations are possible.

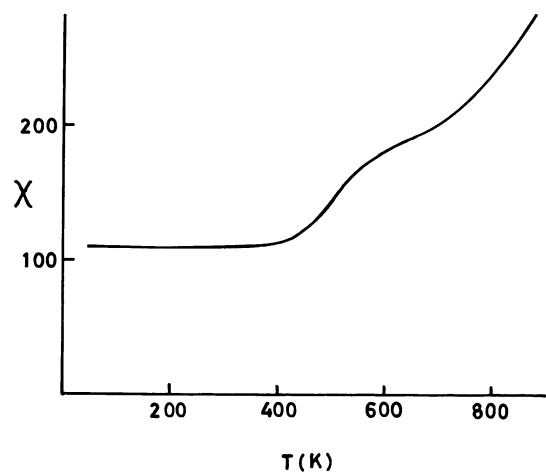


Fig. 7. — Molar magnetic susceptibility $\times 10^6$ in cgs units.

Finally, we ask how the transition-temperature should be affected by charged impurities, or an impurity band. If the number of such impurities is n_0 , the $n^{1/3}$ in (2) should become $(n + n_0)^{1/3}$, but the kinetic energy and entropy terms will not be affected. We therefore estimate that the transition-temperature should be lowered by

$$\delta T/T_c \sim \frac{1}{3} \frac{n_0}{n}.$$

Thus if n is 0.1, and $n_0 \sim 0.05$, we estimate that T_c should be lowered by 1/6, or about 70°. An examination of the results of reference [4] on $(\text{Ti}_{1-x}\text{V}_x)_2\text{O}_3$ suggests that this may be roughly correct.

Acknowledgments. — I am grateful to many colleagues for discussions about this problem, particularly C. Schlenker, J. Dumas, J. Goodenough, J. M. Honig, G. Lucovsky and R. J. Sladek.

References

- [1] LUCOVSKY, G., ALLEN, J. W. and ALLEN, R. (1981), in press.
[2] HONIG, J. M., *Rev. Mod. Phys.* **40** (1968) 748.
[3] DUMAS, J. and SCHLENKER, D., *J. Physique Colloq.* **37** (1976) C4-41; *Phys. Rev. B* **20** (1979) 3913; *J. Phys. C* **12** (1979) 2301.
[4] CHANDRASHEKHAR, G. V., WON CHOI, Q., MOYO, J. and HONIG, J. M., *Mat. Res. Bull.* **5** (1970) 949.
[5] ZEIGER, H. J., *Phys. Rev. B* **11** (1975).
[6] MOTT, N. F., *Philos. Mag.* **20** (1969) 1; *Metal-Insulator transitions* (Taylor & Francis, London) 1974.
[7] ASHKENAZI, J., VINCENT, M. G., YVON, K. and HONIG, J. M., *J. Phys. C* (1981) in press.
[8] CHEN, H. L. S. and SLADÉK, R. J., *Phys. Rev. B* **18** (1978) 6824.
[9] LUCOVSKY, G., *Bull. Am. Phys. Soc.* **23** (1978) 373.
[10] ASHKENAZI, J. and CHUCHENS, T., *Philos. Mag.* **32** (1975) 763.
[11] BRINKMAN, W. F. and RICE, T. M., *Phys. Rev.* **7** (1973) 1508.
[12] SHIN, S. H., CHANDRASHEKHAR, G. V., LOCKMAN, R. E. and HONIG, J. M., *Phys. Rev. B* **8** (1973) 1364.
[13] YAHIA, J. and FREDERIKSE, H. P. R., *Phys. Rev.* **123** (1961) 1257.
[14] GOODENOUGH, J., *Transition Metal Oxides*, in *Progress in Solid State Chemistry*, ed. H. Reiss (Pergamon) 1971, Vol. 5, p. 145.
[15] BARROS, H. L., CHANDRASHEKHAR, G. V., CHI, T. C., HONIG, J. M. and SLADEK, R. J., *Phys. Rev.* **7** (1973) 5747.
[16] LUCOVSKY, G., SLADEK, R. G. and ALLEN, J. W., *Phys. Rev. B* **16** (1977) 5452.
[17] AUSTIN, I. G. and MOTT, N. F., *Adv. Phys.* **18** (1969) 41.
[18] RACCAH, P. N. and MORRADIAN, A., *Bull. Am. Phys. Soc. II* **15** (1970) 327.
[19] DUMAS, J., Thesis, Grenoble (1978), p. 45.
[20] MASSANET, O., SINCE, J. J., MERCIER, J., AVIGNON, M., BUDER, R. and NGUYEN, V. D., *J. Phys. Chem. Solids* **40** (1979) 573.
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