

## Metal-insulator transitions in $\text{VO}_2$ , $\text{Ti}_2\text{O}_3$ and $\text{Ti}_{2-x}\text{V}_x\text{O}_3$

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[Received 23 May 1974]

### ABSTRACT

A discussion is given of metal-insulator transitions in  $\text{VO}_2$ ,  $\text{Ti}_2\text{O}_3$  and also in  $\text{Ti}_{2-x}\text{V}_x\text{O}_3$ , which at low temperatures becomes metallic with increasing  $x$ . Although these are band-crossing transitions, there being no magnetic moments on the metallic ions, a large discontinuity is expected in the number of current-carriers in  $\text{VO}_2$  as the degree of pairing of the V atoms is varied. We relate this to the first-order transition observed as the temperature is raised. In  $\text{Ti}_2\text{O}_3$  electrons in the conduction band appear to be much heavier than holes in the valence band and are probably small polarons. The addition of  $\sim 2\%$  of  $\text{V}_2\text{O}_3$  appears to push  $\text{Ti}_2\text{O}_3$  across the metal-insulator transition, again with a discontinuous change in the number of carriers, the alloy being a semimetal with heavy electrons and light holes. The experiments of Sjöstrand and Keesom (1973) are discussed; the reason why the heavy electron polarons form a degenerate gas at helium temperatures, rather than a Wigner crystallization, is that the Coulomb interaction between them is strongly screened by the light holes. The situation is compared with that in  $\text{Fe}_2\text{O}_4$  and  $\text{Ti}_4\text{O}_7$ .

### § 1. INTRODUCTION

The materials  $\text{VO}_2$  and  $\text{Ti}_2\text{O}_3$  discussed in this paper are both non-metals and not magnetic at low temperatures, and this behaviour can be described formally by a model of non-interacting electrons occupying a full valence band with an empty conduction band. In both materials there is one electron per transition metal ion.  $\text{Ti}_2\text{O}_3$ , which has the corundum structure, undergoes a gradual transition to metallic behaviour as the temperature is raised, which is accompanied by an increase in the  $c/a$  ratio, and this is believed to lead to overlap or near overlap of the valence and conduction bands (Goodenough 1971). On the other hand  $\text{Ti}_2\text{O}_3$  containing a few per cent of  $\text{V}_2\text{O}_3$  is metallic, with a very large linear specific heat (Sjöstrand and Keesom 1973) and low degeneracy temperature ( $\sim 10$  K).  $\text{VO}_2$  in the high-temperature metallic phase has the rutile structure, but at 340 K undergoes a first-order transition to the non-metallic phase in which the vanadium atoms form pairs. A formal treatment of the non-metallic phase in terms of conventional band theory has been given by Caruthers and Kleinman (1973).

The purpose of this paper is to show that neither material can be fully understood without consideration of electron-electron interaction, expressed both through the Hubbard intra-atomic term  $U$  and through the long-range inter-atomic potential energy  $e^2/r_{12}$ ; the latter leads to a discontinuous change

in the number of current carriers at any metal-insulator transition. The proposal for a discontinuous change was first put forward by the present author (1949, 1956, 1961) and Knox (1963) and has been greatly clarified by the recent work of Brinkman and Rice (1973) based on the properties of electron-hole droplets in germanium. The argument of the latter authors can be expressed as follows. Consider any non-metal in which two full and empty bands do not overlap; the bands can be 'Hubbard bands', in which case the band gap is

$$U - \frac{1}{2}(B_1 + B_2),$$

where  $B_1, B_2$  are the band-widths of the two bands and the atoms carry moments; or alternatively they can be bands determined by the crystal structure, as they are in this paper. If, due to a change in the lattice parameters or in the composition, the bands begin to overlap, then a *small* number  $n$  per  $\text{cm}^3$  of free electrons and holes will form. These may crystallize into an excitonic phase, and in fact Kohn (1967) envisaged an infinite series of second-order transitions to more and more complicated excitonic phases leading up to a metal-insulator transition. Brinkman and Rice (1973) on the other hand showed that, if energy surfaces in the  $k$ -spaces are sufficiently anisotropic, the formation of a metallic electron-hole droplet for a given small value of  $n$  will always have lower energy than a uniformly distributed 'crystal' of excitons. For the metal-insulator transition this leads to the following conclusion. As soon as there is small overlap, an electron-hole droplet is formed. But it takes no further energy to increase the number of carriers so that the 'droplet' fills all space. This means that there is a *discontinuous* change in  $n$  from zero to the value at which the energy of the electron-hole gas has its minimum.

If the energy surfaces are isotropic, it is argued that a non-conducting excitonic phase may form, but when the parameters are varied so that overlap between the bands of this phase begins, the energy surfaces will certainly be anisotropic. A *finite* series of excitonic phases, as envisaged by Kohn, is indeed possible, but the series is certain to end with a discontinuous change of  $n$ .

The density at which the electron-hole gas has its minimum energy has been calculated by Brinkman and Rice (1973), Inoue and Hanamura (1973) and Vashishta, Bhattacharyya and Singwi (1973); we give a rough estimate for the isotropic case. The kinetic Fermi energy is

$$2 \times \frac{3}{8} \left( \frac{3}{\pi} \right)^{2/3} \frac{\pi^2 \hbar^2}{2m} n^{2/3}, \quad (1)$$

and the potential energy, assuming a uniform distribution of electrons and holes (Mott and Jones 1936, p. 138), is

$$-1.2e^2/\kappa r, \quad (2)$$

where  $(4\pi/3)r_0^3 = 1/n$ , so that (2) becomes

$$-1.2e^2 n^{1/3} (4\pi/3)^{1/3} / \kappa.$$

The energy has its minimum value when

$$\frac{4}{3} \left( \frac{3}{\pi} \right)^{2/3} \frac{\pi^2 \hbar^2 n^{-1/3}}{2m} = 0.4e^2 n^{-2/3} (4\pi/3)^{-1/3} / \kappa, \quad (3)$$

so that

$$n^{1/3}a_H \simeq 0.1, \tag{4}$$

where

$$a_H = \hbar^2 \kappa / m^* e^2. \tag{5}$$

Here  $m^* = m_e m_h / (m_e + m_h)$ ,  $m_e$  and  $m_h$  being the effective masses of electrons and holes, and  $\kappa$  is a background dielectric constant, the value of which will be discussed below. The use of eqn. (4) gives for the energy per pair

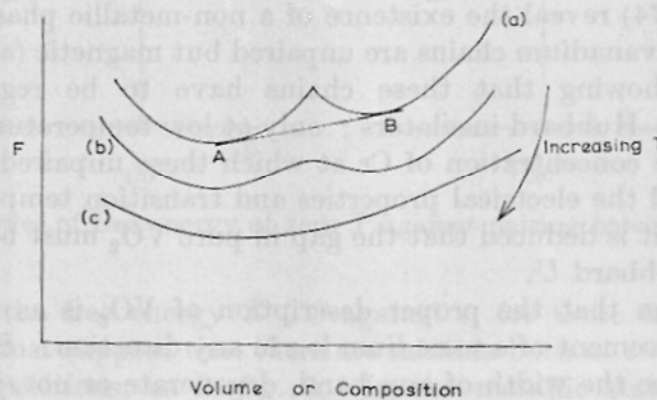
$$-0.3W_0,$$

where  $W_0 = m^* e^4 / 2\kappa^2 \hbar^2$ , and thus not nearly as low as that of an exciton ( $-W_0$ ); but Vashishta *et al.* (1973) find that the inclusion of correlation between electrons and holes may greatly lower the energy of an electron-hole gas, so that it becomes uncertain which is the lower, even for the isotropic case. Doubtless for quite small values of the anisotropy of the energy surfaces, the electron-hole gas has the lower energy. The number on the right of (4) is probably about 0.3 or even larger.

We now discuss further the quantity  $\kappa$ , the 'background dielectric constant'. It is not, for instance in the case of Si:P, the dielectric constant of Si, but the dielectric constant due to transitions between the bands, Hubbard or otherwise. For a transition in a divalent metal such as Yb we may suppose that  $\kappa$  is very large, which is why no discontinuity is observed for this material under pressure (McWhan, Rice and Schmidt 1969, Jullien and Jerome 1971). For Hubbard bands, since transitions from the lower to the upper band involve transference of the electron from one atom to another,  $\kappa$  is not expected to be large, perhaps about two (or twice the dielectric constant of the material in a system with large orbits such as Si:P, cf. Mott 1974 b). For  $d$  bands, where splitting is due to the crystal structure, we believe that the high-frequency dielectric constant  $\kappa_\infty$  will normally be small too, so a large discontinuity in  $n$  is expected.

When there is a discontinuity in  $n$ , the free energy curves plotted against volume (or any other lattice parameter) or composition in an alloy are expected at zero temperature to show a kink, as in fig. 1. This has been pointed out by

Fig. 1



Free energy  $F$  as a function of volume or composition for a metal-insulator transition. (a) At zero temperature. (b) For increasing temperature. The region between A and B is unstable at  $T=0$ .

various authors (Mott 1961, Krumhansl 1965, Thompson 1967). On one side of the kink, the electron-hole gas fills the whole material; on the other side there are no carriers at zero temperature, and a finite gap, equal to the energy calculated without correlation *minus* that required to form a single exciton. Thus a metal-insulator transition, either as a function of composition ( $x$ ) or pressure, must be a first-order transition. For alloys there will be a two-phase region between A and B in fig. 1. The state where the energy of the electron-hole gas has its minimum will be at the 'kink', and can thus be only observed, if at all, in *quenched* unstable alloys.

Finally, there is an important difference between Hubbard bands and those determined by the band structure. In the case of the former, if  $n$  is greater than about  $1/2z$  ( $z$ =coordination number), the antiferromagnetic lattice will disappear (Mott 1971, 1974 a) and *all* the electrons may be regarded as free, the Fermi surface enclosing a corresponding volume. But the gas is highly correlated in the sense first described by Brinkman and Rice (1970), and the electronic specific heat and the Pauli paramagnetism are much enhanced. The quantity  $n$  refers then to the number of doubly-occupied sites. Nothing of the kind occurs when the bands are due to crystal structure, as in the cases discussed here.

## § 2. VANADIUM DIOXIDE

For the metallic rutile phase the calculations of Caruthers and Kleinman (1973) give good agreement with the reflectance data. The electron gas, in contrast to 'metallic'  $V_2O_3$ , is not highly correlated, the enhancement of the susceptibility over that obtained from the calculations of the density of states by these authors being not more than three. Also the susceptibility is much less temperature-dependent. For this reason, following Paul (1970), we think that the entropy of the transition comes mainly from the phonons.

In the low-temperature phase the vanadium atoms are paired; the band-gap is about 0.5 eV, the conductivity usually observed being extrinsic and probably due to electrons excited from a  $V^{3+}$  ion coupled to an oxygen vacancy. While calculations based on the band theory of non-interacting electrons are given by the above authors, this is likely to be a poor approximation (Rice, McWhan and Brinkman 1970), the Hubbard  $U$  playing a large role. The investigations of Pouget, Launois, Rice, Dernier, Gossard, Villeneuve and Hagemmuller (1974) reveal the existence of a non-metallic phase in  $V_{1-x}Cr_xO_2$  in which half the vanadium chains are unpaired but magnetic (above their Néel temperatures), showing that these chains have to be regarded as one-dimensional Mott-Hubbard insulators; only at low temperatures does pairing occur. Since the concentration of Cr at which these unpaired chains form is small ( $\sim 2\%$ ) and the electrical properties and transition temperature are not greatly affected, it is deduced that the gap in pure  $VO_2$  must be mainly determined by the Hubbard  $U$ .

We think then that the proper description of  $VO_2$  is as follows. Let  $\epsilon$  denote the displacement of a vanadium ion in any direction. Such a displacement will decrease the width of any band, degenerate or not, in which the  $d$ -electron moves. Any such narrowing, as in the discussion frequently given of  $V_2O_3$ , will lead to a discontinuous 'Mott' transition to an antiferromagnetic insulator. The gap opened up is  $U-B$ , where  $B$  is the band width. But in

$VO_2$ , in contrast to  $V_2O_3$ , the energy can be lowered slightly by allowing the atoms to form diamagnetic pairs. Each pair should be described by a molecular wave function of the type introduced by London and Heitler (1927) for  $H_2$ , namely in the ground state

$$\psi(1, 2) = a(1)b(2) + a(2)b(1), \quad (6)$$

where  $a(x)$  is the wave function of an electron on atom  $a$ . Any polar term of the type  $Aa(1)a(2)$  will have small amplitude if  $U$  is large, and we assume this to be the case. The first excited state for the pair will have a wave function of the type

$$\psi(1, 2) = a(1)b(2) - a(2)b(1), \quad (7)$$

and the energy gap between these states may well be small ( $\sim 0.1$  eV). A very weak absorption line for this singlet-triplet transition should exist in the far infra-red, if not obscured by the phonon spectrum.

To describe the conduction band, we should introduce the one-electron wave function  $\phi_s(x)$  for a third electron on one of the vanadium pairs denoted by  $s$ . The wave function for the conduction electron is then

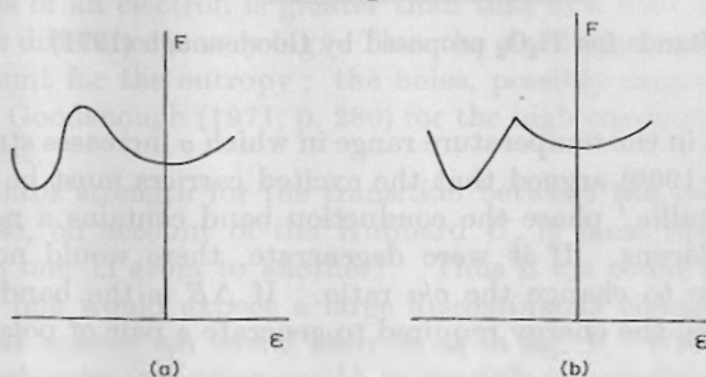
$$\sum_s \exp(ika_s) \phi_s(x).$$

The band gap is

$$U - \frac{1}{2}(B_1 + B_2) + \Delta E,$$

where  $B_1$ ,  $B_2$  are the valence and conduction band widths, and  $\Delta E$  the amount the gap is increased by pairing. We shall not attempt to calculate this, merely assuming that  $\Delta E$  increases as  $\epsilon$ , the displacement of the vanadium atoms from their position in the rutile structure, increases.

Fig. 2



Possible curves of free energy at zero  $T$  against pairing parameter for  $VO_2$ .

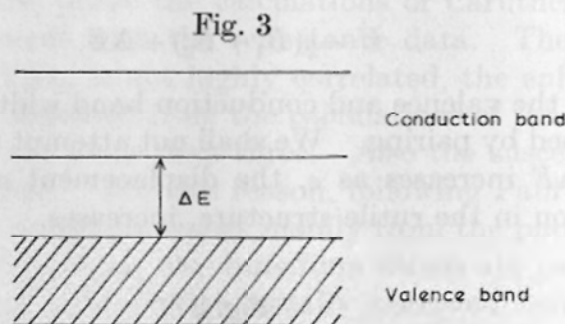
If we plot the free energy  $E-TS$  against  $\epsilon$ , for there to be a first-order transition we must suppose that there are minima both at  $\epsilon = 0$  (rutile) and for the displaced positions, as in fig. 2. In the metallic state, this minimum doubtless occurs because electrons are in the  $\pi^*$  band, which is broad because of interaction with other vanadium ions *via* the oxygen ions. We add however that either for a Mott transition or for a band-crossing transition of this kind a

kink *must* occur in the plot of  $F$  (at zero temperature) as a function of  $\epsilon$  (fig. 2 (b)). The metal-insulator transition as a function of temperature occurs when the (phonon) entropy in the metallic state lowers the minimum at  $\epsilon = 0$ , so that the values of  $F$  for the two minima are the same.

A similar diagram could be drawn for  $V_2O_3$  where  $\epsilon$  would be the value of  $c/a$ . The difference for  $VO_2$  is that the change of  $\epsilon$  at the transition is much larger than that in  $c/a$  in  $V_2O_3$ ; therefore we expect metallic  $VO_2$  to be much further from the metal-insulator transition. The electron gas will thus be much less correlated, as observed. Also we might well expect that, as in  $V_2O_3$  and, as we shall see in the next section,  $Ti_2O_3$ , small additions of impurity would greatly affect the value  $\epsilon$  at which the transition occurs. But in  $VO_2$  this would not necessarily affect the properties so much, again because the two minima are farther from the transition.

### § 3. TITANIUM TRIOXIDE ( $Ti_2O_3$ )

Goodenough (1971) has shown that for the corundum structure a band with one electron per atom will split off below the other d-bands; the gap between it and the upper bands is small, and, as the temperature rises, electrons are excited across it (fig. 3). They show that the gap diminishes with increasing



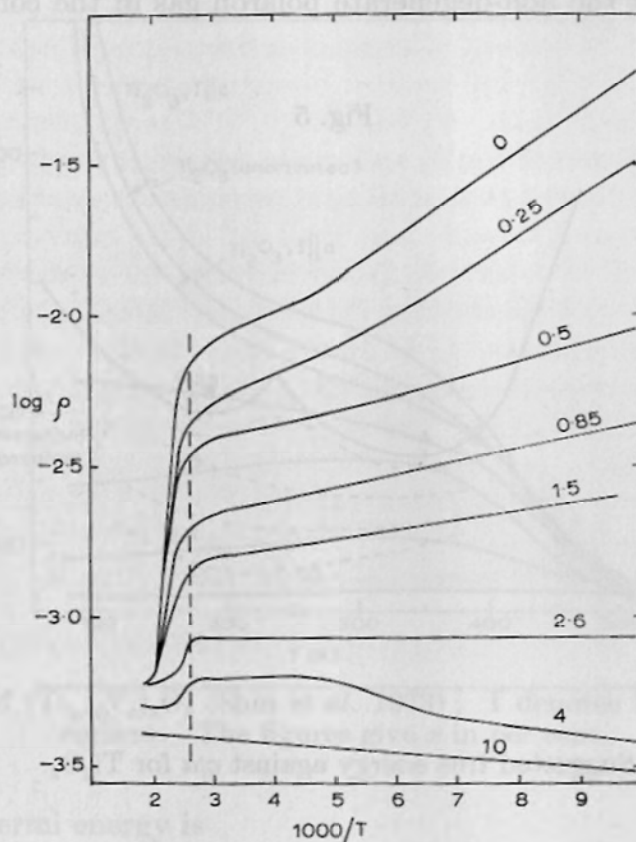
Bands for  $Ti_2O_3$  proposed by Goodenough (1971).

$c/a$ , which occurs in the temperature range in which  $\sigma$  increases strongly (fig. 4). One of us (Mott 1969) argued that the excited carriers must be polarons and that in the 'metallic' phase the conduction band contains a non-degenerate gas of small polarons. If it were degenerate, there would not be enough entropy available to change the  $c/a$  ratio. If  $\Delta E$  is the band gap without polaron formation, the energy required to generate a pair of polarons is

$$\Delta E - E_p - E_p', \quad (8)$$

where  $E_p, E_p'$  are the polaron energies ( $\sim 0.4$  eV). While  $\Delta E$  may be of order  $\sim 1$  eV, (8) can be much smaller, and a small change in  $\Delta E$  due to changing  $c/a$  can make (8) vanish. The number of carriers per metal atom in the 'metallic' phase is deduced from the entropy change and susceptibility to be of order 0.1, and is limited by the fact that, if it became greater than this value, the carriers would compete for polarization energy from surrounding ions, so that the magnitude of  $E_p$  would decrease.

Fig. 4



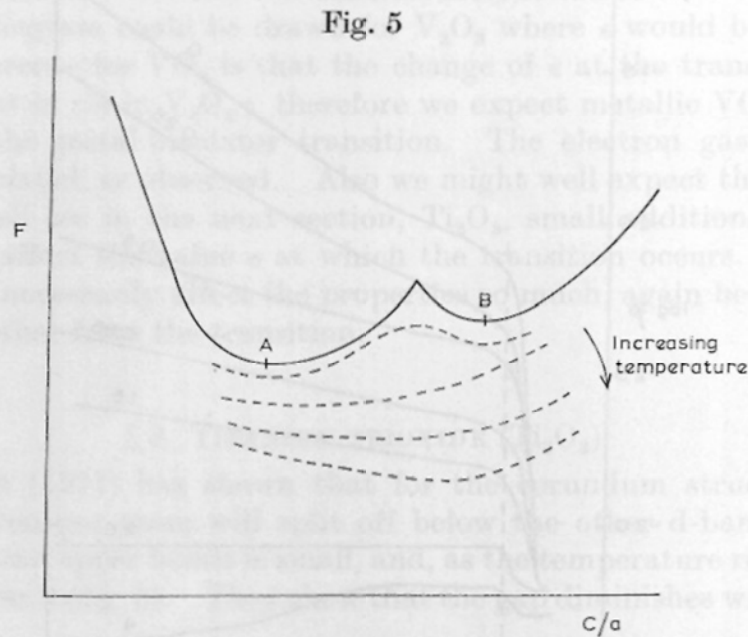
Log resistivity in  $\Omega$  cm of pure and vanadium-doped  $Ti_2O_3$  as a function of  $1000/T$  (Chandrashekar *et al.* 1970). The figures give concentration of  $V_2O_5$  in per cent.

We now think that an improvement in the model would be to assume that the bare mass of an electron is greater than that of a hole, and after polaron formation the difference is very big. Thus the electrons form a non-degenerate gas and account for the entropy; the holes, possibly degenerate, account as suggested by Goodenough (1971, p. 280) for the high conductivity and positive Hall coefficient.

The oscillator strength for the transition between the two bands must be small, because, on account of the Hubbard  $U$ , it must involve moving the electron from one Ti atom to another†. Thus if  $c/a$  could be varied at zero temperature, one would expect a large *discontinuous* change in  $n$ ; the free energy plotted against  $c/a$  would then be as in fig. 1. With increasing temperature a first-order transition would be possible in principle, if B drops more rapidly than A, and, at some temperature before the maximum in the curve disappears, if B has the same free energy as A. The reason (in contrast with  $VO_2$ ) why this does not happen is, we suggest, that the free-energy curves are as in fig. 5, the re-entrant part disappearing before the minimum at A (metallic) drops below that at B (non-metallic). We do not suppose that the phonon

† If it were not,  $\kappa_\infty$  would be large and the polaron energy  $\frac{1}{2}(e^2/r_p)(\kappa_\infty^{-1} - \kappa^{-1})$  could not be large.

spectrum at A is appreciably softer than at B; the entropy driving the transition will be that of the non-degenerate polaron gas in the conduction band of  $\text{Ti}_2\text{O}_3$ .



Suggested free energy against  $c/a$  for  $\text{Ti}_2\text{O}_3$ .

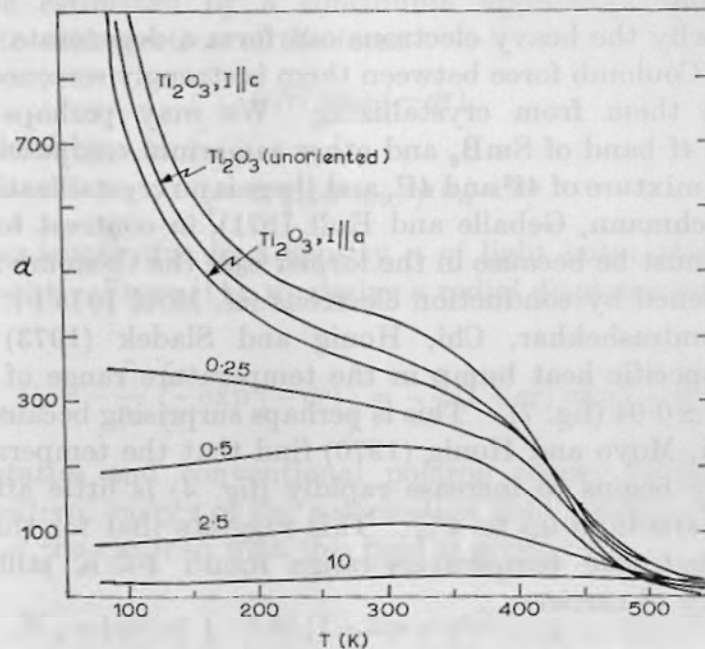
We turn now to the remarkable results of Sjöstrand and Keesom (1973) on  $\text{Ti}_2\text{O}_3$  containing a few per cent of  $\text{V}_2\text{O}_3$ . These alloys are metallic; there is a very large linear electronic specific heat, saturating at a few degrees. The saturation value gives the number of carriers, assuming each to make a contribution  $(3/2)k$ , and gives a density of the order  $10^{20}$ – $10^{21}$   $\text{cm}^{-3}$ , about 0.4 per V atom, and the linear part shows that the band-width has to be about 0.01 eV, corresponding to an effective mass  $\sim 1000m_e$ . Shin, Chandrashekar, Loehman and Honig (1973) measure the thermopower  $\alpha$  of these crystals (fig. 6). Metallic behaviour, or at any rate a value of  $\alpha$  that does not rise with decreasing temperature at low  $T$ , sets in at  $\sim 0.25$  atomic per cent of  $\text{V}_2\text{O}_3$ . If the thermopower is written as  $(k/e) \ln(N/n)$ , as for a non-degenerate gas with a fraction  $n/N$  of vanadium sites occupied, then a constant value of  $\alpha$  equal to  $300 \mu\text{V}/^\circ\text{K}$  implies  $\ln(N/n) \sim 4$ , or  $n \simeq 10^{-2} N$ , which agrees with the value deduced directly from the specific heat.

The addition of  $\text{V}_2\text{O}_3$  is known to increase  $c/a$ ; it will thus reduce the band gap. We thus expect a discontinuous change from a non-metal to a semimetal with a density of carriers given by (4). Since this depends on  $m^*$ , it will depend on the lighter of the two carriers.

A discontinuous formation of a semimetal with increasing  $\text{V}_2\text{O}_3$  content is therefore to be expected. The difficulty, however, in understanding these results is the following. The addition of small amounts of  $\text{V}_2\text{O}_3$  introduces free carriers, of which the number  $n$  is known from the saturation value of the specific heat; it is less than the concentration of vanadium but increases with it. The linear specific heat  $\gamma T$  gives  $m_{\text{eff}}$ , since

$$\gamma = \frac{1}{2} \pi^2 n k^2 / E_F,$$

Fig. 6



Thermopower  $\alpha$  of  $(Ti_{1-x}V_x)_2O_3$  (Shin *et al.* 1973); I denotes the direction of the current. The figures give  $x$  in per cent.

where  $E_F$ , the Fermi energy is

$$E_F = (3n/\pi)^{2/3}(\hbar^2\pi^2/2m_{\text{eff}}).$$

$\gamma$  is thus proportional to  $n^{1/3}m_{\text{eff}}$ , and very large values of  $m_{\text{eff}}$  of order  $1000m_e$  are required to account for the observed values of  $\gamma$ . Moreover  $\gamma$  is observed to decrease with increasing  $n$ , so  $m_{\text{eff}}$  must decrease with  $n$  faster than  $n^{-1/3}$ . But for a metallic electron gas to remain metallic and not crystallize, some condition ought to be satisfied of the type

$$n^{1/3}a_0 \simeq 0.1, \quad (9)$$

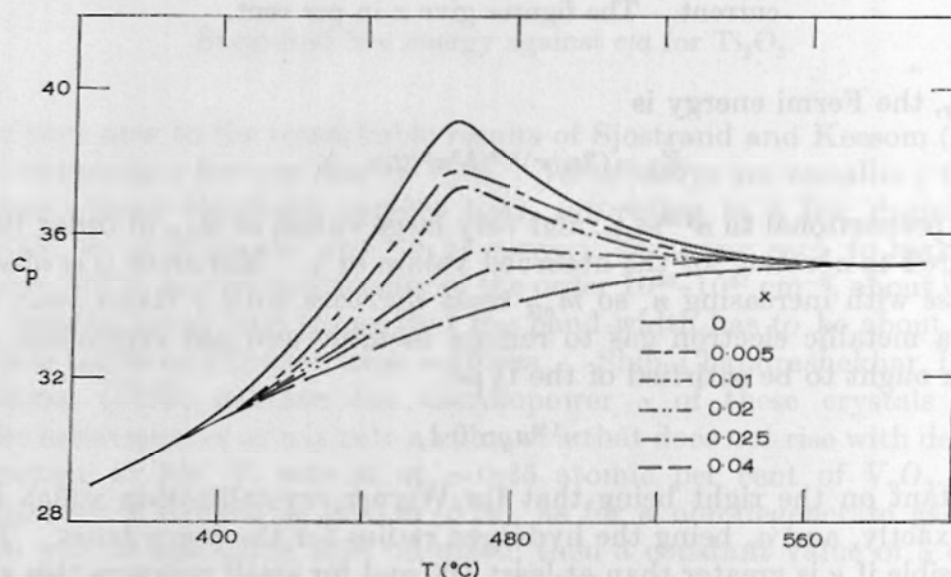
the constant on the right being that for Wigner crystallization which is not known exactly, and  $a_0$  being the hydrogen radius for the *heavy* holes. This is only possible if  $\kappa$  is greater than at least 100 and for small polarons this should be the *static* dielectric constant. Now degenerate gases of small polarons are known, slightly reduced  $SrTiO_3$  for example (Mott 1967, 1974 a), but here the background dielectric constant  $\kappa$  in these ferroelectric materials is very large. For  $Ti_2O_3$ , on the other hand, Goodenough (private communication) has deduced from the infra-red absorption that  $\kappa$  is only about 16, so another way of screening the interaction must be found. We think that what has happened in the alloys is that the addition of  $V_2O_5$  has caused the two bands to overlap, probably with a discontinuous change in the number of carriers (though this is not essential to our argument). Goodenough (1971) has deduced from the comparatively high conductivity of these alloys and positive Hall coefficient (Honig, Van Zandt, Reed and Sohn 1969) that the holes are much lighter than the electrons, and both in pure  $Ti_2O_3$  as we have already stated, and in the alloys the holes carry most of the current. We suppose again that the bare

masses differ considerably and that the difference is greatly enhanced by polaron formation.

The reason why the heavy electrons can form a degenerate electron gas is clearly that the Coulomb force between them is strongly screened by the holes, which prevents them from crystallizing. We may perhaps compare the situation in the 4f band of  $\text{SmB}_6$  and other samarium compounds where the f band contains a mixture of  $4f^6$  and  $4f^7$ , and there is no crystallization (Nickerson, White, Lee, Bachmann, Geballe and Hull 1971), in contrast to  $\text{Fe}_3\text{O}_4$ , where there is. This must be because in the former case the Coulomb forces between  $4f^7$  ions are screened by conduction electrons (cf. Mott 1974 b).

Barros, Chandrashekhar, Chi, Honig and Sladek (1973) find that in  $\text{Ti}_{2-x}\text{V}_x\text{O}_3$  the specific heat bump in the temperature range of the transition disappears for  $x \simeq 0.04$  (fig. 7). This is perhaps surprising because Chandrashekhar, Won Choi, Moyo and Honig (1970) find that the temperature at which the conductivity begins to increase rapidly (fig. 4) is little affected by concentrations of vanadium up to 4%. This suggests that for this value of  $x$  a transition through the temperature-range round 400 K still produces an enhanced density of carriers.

Fig. 7



Specific heat bump in  $(\text{Ti}_{1-x}\text{V}_x)_2\text{O}_3$ ;  $C_p$  is in  $\text{cal mol}^{-1} \text{K}^{-1}$  (Barros *et al.* 1973).

#### § 4. CHANGE OF EFFECTIVE MASS WITH VANADIUM CONCENTRATION

Next we discuss the apparent decrease in the effective mass of the heavy particles in  $\text{Ti}_{2-x}\text{V}_x\text{O}_3$  with increasing  $x$ . This clearly follows from the assumption that they are dielectric polarons and that the Coulomb force round each electron is screened by the holes; the effective mass is of the form (Austin and Mott 1969)

$$\sim 3m_e \exp(W_p/\frac{1}{2}\hbar\omega), \quad (10)$$

where  $W_p$  is the polaron hopping energy. The electron can polarize the medium only inside the screening radius, which decreases with increasing concentration of the lighter carriers, namely the holes.

Following Austin and Mott, we assume that the small polaron binding energy can be estimated by a continuum approximation. We take the potential due to each electron of the form

$$(e/r) \exp(-qr), \quad (11)$$

where  $q^{-1}$ , defined by

$$q^{-1} = \frac{1}{2}(\kappa\hbar^2/me^2)^{1/2}n^{-1/6}, \quad (12)$$

is the screening length due to a density  $n$  of light holes, and  $\kappa$  is the static dielectric constant. From (11), we derive a radial displacement field (Fröhlich 1954)

$$D_r = -\frac{\partial}{\partial r} \left\{ \frac{e}{r} \exp(-qr) \right\} = -\frac{e}{r} (1+qr) \exp(-qr). \quad (13)$$

Using electrostatics and conventional polaron theory (Fröhlich 1954), the sum of the (positive) energy of the polarization field and the (negative) energy of interaction of the electron with this field is given by

$$\begin{aligned} W_p &= \frac{1}{2}(e^2/\kappa) \int_{r_p}^{\infty} r^2 dr (1+2qr+q^2r^2) \exp(-2qr)/r^4 \\ &= \frac{1}{2}(e^2/\kappa)2q \int_z^{\infty} x^{-2} dx e^{-x}(1+x+\frac{1}{4}x^2), \end{aligned} \quad (14)$$

where  $r_p$  is the polaron radius,  $z=2qr_p$ , and  $\kappa_p^{-1}=\kappa_{\infty}^{-1}-\kappa^{-1}$  and where  $\kappa_{\infty}$  is the high-frequency dielectric constant.

Now

$$\int_z^{\infty} x^{-n} e^{-x} dx = z^{-(n-1)} E_n(z),$$

where  $E_n(z)$  is the exponential integral† of argument  $n$ .

Thus,

$$-W_p = \frac{1}{2}(e^2/\kappa_p r_p) \{ E_2(z) + zE_1(z) + \frac{1}{4}ze^{-z} \}.$$

Now from the recurrence relations for the exponential integrals,

$$E_2(z) = e^{-z} - zE_1(z),$$

it follows that

$$-W_p = \frac{1}{2}(e^2/\kappa_p r_p) e^{-z} (1 + \frac{1}{4}z).$$

In the limit of zero screening,  $z \rightarrow 0$ , this reduces to

$$-W_p^{(0)} = \frac{1}{2}(e^2/\kappa_p r_p)$$

as it must. Thus (Austin and Mott 1969)

$$\frac{m_{\text{eff}}}{m} = \exp(W_p/\hbar\omega) = \exp \left\{ \frac{W_p^{(0)}}{\hbar\omega} (1 + \frac{1}{4}z) e^{-z} \right\}, \quad (15)$$

where  $m$  denotes the band mass and  $\omega$  is the optical phonon frequency of  $Ti_2O_3$ .

† See *Handbook of Mathematical Functions*, edited by M. Abramowitz and P. H. Keesom (National Bureau of Standards).

We now ask whether (15) can account for the low-temperature specific heat data of Sjöstrand and Keesom (1973). First, as noted previously, the slope of the low-temperature specific heat  $\gamma$  varies with  $m_{\text{eff}}$  as

$$\gamma \sim m_{\text{eff}} n^{1/3}. \quad (16)$$

Sjöstrand and Keesom quote carrier concentrations  $n \sim 10^{20} \text{ cm}^{-3}$ . They also state that when the concentration of vanadium is increased by a factor of 1.86 (from  $2.1 \times 10^{22} \text{ mol}^{-1}$  to  $3.9 \times 10^{22} \text{ mol}^{-1}$ ),  $\gamma$  decreases from 78 to 56  $\text{J mol}^{-1} \text{ K}^{-2}$ , a factor of 0.72. Assuming that the concentration  $n$  is also increased by 1.86, this would give a factor of  $(1.86)^{1/3} = 1.23$ , leaving a factor of 0.585 to be accounted for in  $m_{\text{eff}}$ .

Taking  $n = 10^{20} \text{ cm}^{-3}$ ,  $\kappa = 14$ ,  $r_p = 3 \text{ \AA}$ , and a coupling constant  $W_p^0/\hbar\omega = 10$ , we find  $q^{-1} = 20 \text{ \AA}$ ,  $z = 0.3$ , and, from (15), that  $m_p/m = \exp(7.96)$ . On the other hand, for  $n = 1.86 \times 10^{20} \text{ cm}^{-3}$ , we calculate  $q'^{-1} = 18.0 \text{ \AA}$ ,  $z' = 0.36$ , and  $m_p'/m_p = \exp(7.6)$ . This accounts for a decrease in mass of

$$m_p'/m_p = \exp(-0.36) = 0.7,$$

in fair agreement with the observations in view of the approximate nature of the calculation and arbitrary choice of coupling constant.

#### § 5. SOME RELATED FORMS OF POLARON BEHAVIOUR

In this paper we have suggested :

- (a) That  $\text{VO}_2$  can be considered as a 'Mott' transition, the formation of diamagnetic pairs being not the true cause of the insulating state.
- (b) That  $(\text{Ti}_{1-x}\text{V}_x)_2\text{O}_3$  is to be described as a degenerate gas of small electron polarons, Wigner or Verwey crystallization being prevented by screening by much lighter holes.

It seems useful to compare these models with what happens in some other materials.

As regards (a), in metal-ammonia solutions on the non-metal side of the transition the formation of diamagnetic pairs (dimers) is well known. Another example is  $\text{Ti}_4\text{O}_7$  (Marezio, McWhan, Dernier and Remeika 1973, Schlenker, Lakkis, Coey and Marezio 1974). In this material half the sites are occupied by  $\text{Ti}^{3+}$ , half by  $\text{Ti}^{4+}$ . Above 150 K, the material is 'metallic', the sites being occupied by  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  at random. Below 150 K they apparently form diamagnetic pairs distributed at random and moving with a hopping activation energy of polaron type. Below 130 K there is a drop in the conductivity without any change in the susceptibility (Bartholomew and Frankl 1969); the diamagnetic pairs apparently 'crystallize', as carriers do in  $\text{Fe}_3\text{O}_4$  at the Verwey transition.

What is remarkable in both these cases is that the pairing takes place in spite of the Coulomb repulsion between the carriers. This can only mean that the Coulomb energy is greatly reduced by the *static* dielectric constant, which determines the interaction between small polarons.

As regards (b), examples in which a gas of polarons crystallizes at low temperatures are provided by  $\text{Fe}_3\text{O}_4$  and  $\text{Ti}_4\text{O}_7$  already mentioned. An example of a degenerate gas where a very high dielectric constant prevents

either Wigner crystallization or condensation onto donors is provided by reduced  $SrTiO_4$  (cf. Mott 1967, 1974 a), where the background dielectric constant is about 1000.

Another material where the explanation of its properties involves pair formation is  $V_7O_{13}$ , discussed by Gossard, Remeika, Rice, Yasuoka, Kosuge and Kachi (1974). This material is metallic at all temperatures and has thermopower and conductivity similar to metallic  $V_2O_3$ , but a very high and temperature-dependent susceptibility with a Néel point at  $\sim 60$  K. As these authors state, the conductivity and thermopower require a band-width of  $\sim 1$  eV but the magnetic properties demand  $\sim 0.01$  eV. Clearly our overlapping band model as for  $Ti_{1-x}V_xO_2$  is not appropriate here. We suppose however that *some*—perhaps most—of the  $V^{3+}$  ions form pairs with spins aligned *parallel*, so that each pair has a moment. This could be possible for degenerate states. These pairs are supposed to distort the lattice, so that each forms a molecular polaron, which should give a large mass enhancement of order  $\exp(+W_H/\frac{1}{2}\hbar\omega)$ . These will interact through *RKKY* coupling, give antiferromagnetic ordering with a low Néel temperature and a very temperature-dependent susceptibility above it. But we cannot assume that all the  $V^{3+}$  ions form pairs, or the remaining  $V^{4+}$  ions would not be metallic, unless they are on the metallic side of a Mott transition, which seems unlikely. We must assume that a dynamic equilibrium is reached in which some  $V^{3+}$  ions are paired and some not; we assume that if they were all paired the Fermi energy of the 'metal' would not have the value which minimizes the total energy. Thus the paired  $V^{3+}$  ions must order in space at a distance from each other perhaps incommensurate with the lattice, presumably giving a sort of Wigner crystallization.

Gossard *et al.* report that the Curie constant  $C$  is close to that which could be calculated for two  $V^{3+}$  and five  $V^{4+}$  ions, i.e.

$$C \propto 5 \times \frac{3}{2} + 2 \times 2 = 7\frac{3}{2}.$$

If we supposed the  $V^{4+}$  to be non-magnetic and the  $V^{3+}$  to form pairs with parallel spins, we should have

$$C \propto 1 \times 12 = 12,$$

which is as we expect too big, indicating that about  $\frac{1}{3}$  of the  $V^{3+}$  states are mobile, making the surrounding gas metallic.

#### ACKNOWLEDGMENTS

We are grateful to J. Goodenough, T. M. Rice and A. Zylbersztein for discussions about the subject matter of this paper.

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