Thermodynamic analysis of the metal-insulator transitions in V_2O_3 alloy systems

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Abstract. An overview is presented concerning the entropies (ΔS) and enthalpies (ΔH) associated with metal-insulator transitions in the $(V_{1-x}M_x)_2O_3$ M = Al, Cr, Ti systems, $0 \leqslant x \leqslant 0.12$ and in non-stoichiometric $V_{2(1-y)}O_3$, $0 \leqslant y \leqslant 0.01$. The recent literature and new data are analyzed with respect to gradiations in ΔH and ΔS with x or y, and their implications concerning the mechanism of the transitions. A revised phase diagram is presented.

Keywords. Metal-insulator transitions; V_2O_3 alloys; heat capacity; phase diagram; thermodynamic analysis; entropy; enthalpy; non-stoichiometry.

1. Introduction

The metal-insulator transitions in V_2O_3 and its alloys with Ti_2O_3, Al_2O_3, Cr_2O_3 or V_3O_5 have long presented a challenging testing ground for various theories concerning their origin. This subject has been reviewed several times (Goodenough 1967; Rao and Rao 1970; Honig and van Zandt 1975; Rao and Rao 1978) in articles that are now somewhat out of date; the various proposed transition mechanisms are also briefly cited in a recent article on the electrical properties of the $(V_{1-x}Cr_x)_2O_3$ system (Kuwamoto *et al* 1980).

Up to now attention has been focussed on changes in electrical properties concomitant to these transformations; but little effort has been devoted to a study of the corresponding thermodynamic properties. In this paper we cite briefly some past work in this area and then discuss new developments.

It is necessary first to review the basic phenomenology of the system whose study was initiated by McWhan and coworkers (McWhan *et al* 1969; McWhan and Remeika 1970). In figure 1 is shown a schematic diagram of log ρ vs $1/T$, where ρ is the electrical resistivity and T, the absolute temperature. Several regimes (groupings) may be distinguished.

1.1 *Pure V_2O_3 or its extremely dilute alloys:*

At low temperature, the solid is an antiferromagnetic insulator (AFI); with rising T there occurs a first order transition to a paramagnetic metal (M) at approximately
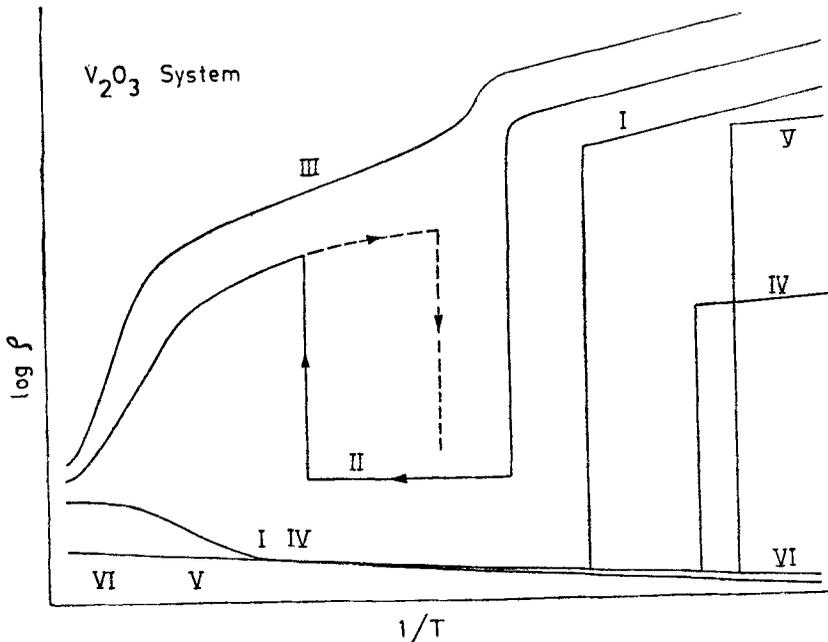
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Figure 1. Schematic diagram showing six regimes for the variation of electrical resistivity (ρ) of V_2O_3 based alloys with temperature (T) as a plot of $\log \rho$ vs. $1/T$.

170 K; an anomalous rise in resistivity is encountered in the region of 350-600 K, beyond which a second metallic phase M' is formed.

1.2 *The $(V_{1-x} Cr_x)_2O_3$ or $(V_{1-x} Al_x)_2O_3$ system with $0\cdot004 < x < 0\cdot018$ which, with rising T, exhibits three transitions:*

One at low temperatures corresponding to the AFI–M transformation; a second, at intermediate temperatures, which corresponds to a sudden transformation from the metallic, M, to a paramagnetic insulating, I, phase; and a third transition from I to M', over a wide temperature range $200 < T < 650$ K. With increasing x, the resistivity of the metallic phase increases by several orders of magnitude and the temperature range over which it is stable shrinks greatly.

1.3 *The $(V_{1-x}Cr_x)_2O_3$ or $(V_{1-x}Al_x)_2O_3$ system with $0\cdot018 < x < 0\cdot12$, in which the M phase is now absent:*

A residual AFI–I transition is encountered at low temperature, and a gradual transformation from the I to the M' phase occurs as the temperature is raised.

1.4 *The $(V_{1-x} Ti_x)_2O_3$ system with $0 < x < 0\cdot06$:*

Here the resistivity jump of the AFI–M transition regime (I) gradually decreases and the transition temperature shifts to lower T with increasing x; the high-temperature anomaly of regime (I) is also gradually suppressed.

1.5   *The $V_{2(1-y)}O_3$ system, with* $0 < y \leqslant 0.01$, which is similar to regime (IV) except that the size of the resistivity discontinuity grows with y.

1.6   *Alloys of V_2O_3 containing more than 6 mol% Ti_2O_3, or V_2O_3 at hydrostatic pressure exceeding 26 kb, or non-stoichiometric V_2O_3 for which* $y > 0.01$:

These conditions lead to the formation of a metallic phase M which exhibits no transitions.   It should be clearly noted that the 'metallic' phases described above are unusual in that their resistivities ρ_m are very high, falling in the range $10^{-4} < \rho_m < 10^{-1}$ ohm cm, depending on the regime.

The above results have recently been rationalized (Kuwamoto *et al* 1980) using the band structure diagram schematized in figure 2, showing a density-of-states (DOS) curve for the band of primarily d-character.   The scheme is loosely based on actual band structure calculations published in the literature (Ashkenazi and Weger 1976; Castellani *et al* 1978).   It depends on the presumption that the Fermi level passes through or very close by a deep minimum in the DOS; (other minima occur elsewhere in the DOS curve but their presence is irrelevant to the discussion at hand).   The resistivity for the M phase is then governed (Wilson 1958) by $D(\epsilon_F)$, the DOS at the Fermi level ϵ_F, represented by the arrow in figure 2(a).   As Cr or Al is added, the
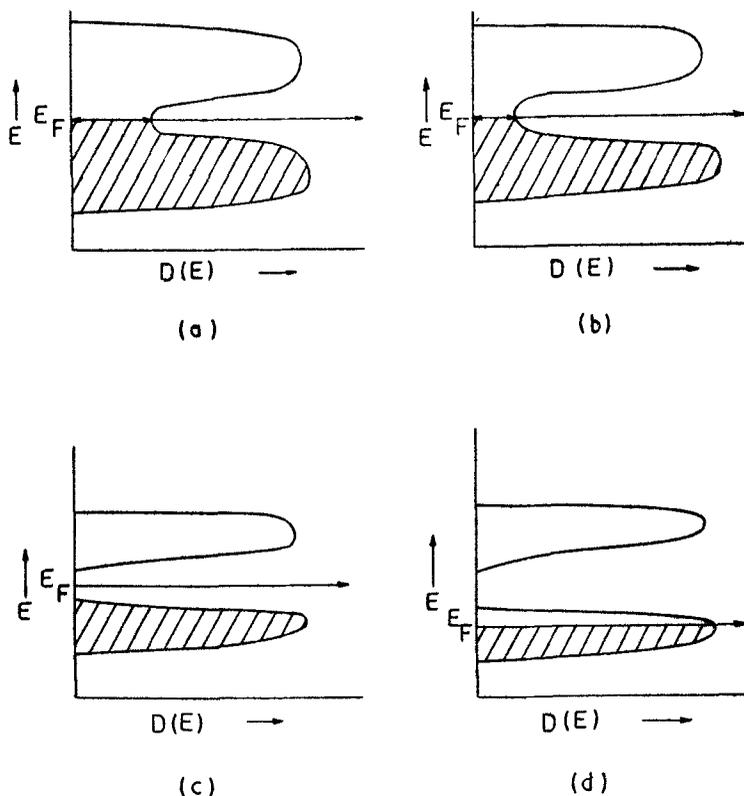

Figure 2.   Schematic density-of-states (DOS) curve for the band structure of V_2O_3 and its alloys.   (a) DOS for pure V_2O_3.   (b) DOS for Cr-doped or Al-doped V_2O_3 at dilute alloy concentrations.   (c) DOS for Cr-doped or Al-doped V_2O_3 at higher concentration levels.   (d) Effect of addition of Ti or excess oxygen.   Shaded regions represent occupied electron states.

band narrows, since a corresponding number of V atoms and their electrons are displaced from the lattice; the alloying material acts as a diluent. The d-like band thus shrinks in width without altering the location of the Fermi level and the minimum in the DOS deepens, as in figure 2(b); this explains the rapid rise in ρ_M with increasing x at fixed T. Ultimately, addition of sufficient Cr or Al opens up a band gap, as shown in figure 2(c); this is consistent with grouping (III) in 1·3. On the other hand, addition of Ti or of excess O leads to the introduction of holes, and thereby lowers the Fermi level progressively away from the deep minimum, as shown in figure 2(d). At the same time, the interactions leading to antiferromagnetic ordering are disturbed and ultimately destroyed when V is replaced by Ti or by cation vacancies; this lowers the M-AFI transition temperature. With sufficient doping, the Fermi level drops well inside the lower portion of the d-band; any opening of the band gap in the DOS is now irrelevant; the material is metallic over the entire temperature range. This rationalizes regions (IV), (V) and (VI) in figure 1.

The gradual changeover from I to M' with rising temperature for alloys of fixed composition in regimes (II) or (III) may be explained as follows: Consider first the M-I transition when the gap opens up, all electrons initially in the immediate vicinity of the Fermi level are displaced downward in energy. The necessary lattice displacements for gap formation are facilitated by the increased phonon density with rising T. However, with further rise in temperature, an increasing fraction of charge carriers is thermally promoted across the gap, thus counteracting the energy reduction of the electron population when the gap was initially created. Now it is energetically more favourable for the lattice to re-arrange itself so as to gradually close the gap and to revert to a state M' rather similar to M.

While the general features of the V_2O_3 system may be rationalized by the above model a detailed understanding of the underlying transition mechanisms is still lacking. Therefore, it seems appropriate to undertake careful thermodynamic studies which provide fundamental information for characterizing any transformation. This task was undertaken because prior work in this area has been surprisingly spotty and not always concordant. Only limited information was available for pure V_2O_3 and virtually no heat capacities or enthalpies of transition had been measured for any V_2O_3 alloys, except in the cryogenic temperature range (McWhan *et al* 1973b).

2. Heat capacity of pure V_2O_3

Heat capacity C_p measurements for pure V_2O_3 are at variance. Jaffray and Lyand (1952) detected a very large specific heat anomaly near 520 K which had not been noted in earlier measurements by Cook (1947). Accordingly, C_p was remeasured by us between 90 and 700 K (Keer *et al* 1977); no unusual features were detected above 200 K. However, Coey and coworkers (Coey *et al* 1976; Coey 1977) did note a very slight anomaly in the heat capacity above room temperature, coincident with the anomalous resistivity change exhibited by pure V_2O_3 in that range. Also, Khlyustov *et al* (1973) reported on heat capacity measurements centred primarily on the low temperature transition. The various results published in the literature, together with the transition temperatures are assembled in table 1. It is noteworthy that the result by Anderson (1936), $\Delta H_t = 2890$ J/mol V_2O_3, lies significantly higher, and that the value cited by the Russian group (Khlyustov *et al* 1973), $\Delta H_t = 1490 \pm 10$ J/mol V_2O_3, lies significantly lower than values reported by all other investigators.

Table 1. Compilation of thermodynamic data pertaining to the low-temperature AFI-*M* transition in V_2O_3.

Year		Heating cycle			Cooling cycle		
		T_l (K)	ΔH_l (J/mol)	ΔS_l (J/mol–)	$\overline{T}_l$ (K)	ΔH_l (J/mol–K)	ΔS_l (J/mol–K)
1936	..	168	2890	17.16			
1973	..	168	1490	8.86			
1973	..	168	1730	10.30			
1976 ⎱ 1977 ⎰		164	1910	11.63			
1976	..	168–173	1950–2025	11.60–11.82	150–152	1995–2100	13.67–13.82
1976	..				152	1965	12.93
1977	..	173	1995–2025	11.53–11.70			
1980	..	172*	1990–2035*	11.50–11.83*			
					152+	1758+	10.57+

* Measurements performed on commercial DSC-2 instrument, fast scan.
+ Measurements performed on relaxation calorimeter.

ΔH_l is clearly dependent on the thermal history and state of subdivision of the samples, but [with the exception of ΔH_l quoted by Anderson (1936) and Khlyustov *et al* (1973)] generally falls within a range 1900–2025 J/mol V_2O_3 in heating cycles and in the range 1990–2100 J/mol V_2O_3 in cooling cycles.

One criterion against which all these results may be judged is their conformity with the Clausius-Clapeyron equation,

$$dT/dp = \Delta V/\Delta S = T\Delta V/\Delta H. \tag{1}$$

It should first be noted that several erroneous values for ΔH or ΔS have been reported in the literature based on an incorrect determination of ΔV. The correct value (McWhan and Remeika 1970) is $\Delta V = 1\cdot 5$ Å^3 per unit cell, which represents a change of approximately $1\cdot 4\%$ of the average volume of V_2O_3—an enormous volume change for any transition. The value of dT/dp has been measured twice, yielding $-3\cdot 1\times 10^{-3}$ (Minomura and Nagasaki 1964) and $-3\cdot 78\times 10^{-3}$ (Feinleib and Paul 1967) deg/bar respectively. Other estimates of dT/dp may be obtained from published diagrams (McWhan and Remeika 1970; Kuwamoto *et al* 1980); these fall in the range $-3\cdot 5\times 10^{-3}$ to $-4\cdot 2\times 10^{-3}$ deg/bar. Inserting the values $dT/dp = -3\cdot 78\times 10^{-3}$ deg/bar and $\Delta V = 1.5$ Å^3 into (1) yields $\Delta S_l = S_M - S_{AFI} = 10.97$ J/mol–K for the low temperature transition.

Judged against this standard, the ΔS_l values of Anderson (1936) and Khlyustov *et al* (1973) appear appreciably off the mark. The remaining ones taken with rising temperature fall better in line with the Clausius-Clapeyron equation; most of these data were gathered on a commercial DSC-2 equipment. Our recent measurements, cited below, are obtained in a heating cycle by use of a relaxation calorimeter; these lead to the result $\Delta S_l = 10.6$ J/mol V_2O_3-K, fairly close to the anticipated value.

All ΔH_l values measured on cooling cycles were generally larger; together with a lower transition temperature T_l due to hysteresis effects, the calculated ΔS_l was usually greater than that found for heating cycles. It is possible that the high ΔH_l and low T_l values on cooling are due to the necessity of considerably overdriving the system in order to initiate a transformation to an expanded phase with an appreciably larger volume. One would then not deal with an equilibrium situation, in which case use of (1) in the analysis of these data would be inappropriate.

It should also be noted that, in most of the specific heat or DSC measurements on pure V_2O_3, no thermal anomaly was detected for the high temperature electrical anomaly of regime (I). However, Coey and coworkers (Coey *et al* 1976; Coey 1977) obtained a value of $\Delta H_h = 0.3$ J/mol for this gradual transformation in the range of 400 to 550 K. This is an important finding whose significance will be discussed later.

3. $(V_{1-x}Al_x)_2O_3$ and $(V_{1-x}Cr_x)_2O_3$ alloy systems

As already remarked, no heat capacity measurements seem to have been carried out on the $(V_{1-x}M_x)_2O_3$ alloy systems, M = Al, Cr, prior to the Purdue work. These particular investigations will be described under two headings:

3.1 *Low temperature transition*

The low-temperature $(L$-$T)$ studies, corresponding to the AFI-*M* or AFI-*I* transitions of groups (II) or (III) and described in Keer *et al* (1977) and Kuwamoto *et al* (1976a) are summarized in figure 3 which depicts the average transition temperature $\bar{T}_l$ and the enthalpies of transition ΔH_l for the Al- and Cr-alloys systems in the range $0 \leqslant x \leqslant 0.12$. It is seen that $\bar{T}_l$ is closely concordant for both sets of alloys, passing through a slight maximum at $x = 0.025$. The large vertical bars indicate the temperature range over which the DSC scans exhibit a peak. It should be noted that $x \geqslant 0.02$ a secondary peak began to show up as a shoulder in the DSC scans which became more pronounced with increasing x, at the expense of the principal peak.

The trends for ΔH_l vs. x of figure 3 are similar for both types of alloys in that the enthalpies peak between 1 to 1.5 mol% for alloy systems belonging to regime (II). As x is increased beyond the stability range of the metallic phase, ΔH_l drops off significantly for all alloy systems belonging to group (III). The variation of ΔH_l with x is considerably smaller for the Cr- than for the Al-alloys. This represents one of the few instances where a clear distinction can be drawn between the $(V_{1-x}Al_x)_2O_3$ and $(V_{1-x}Cr_x)_2O_3$ series.

One should note that the very abrupt change in electrical properties in passing from regime (II) to regime (III) in the AFI transition is not reflected by any comparable discontinuity in ΔH_l. This suggests that the thermodynamics of the L-T transition
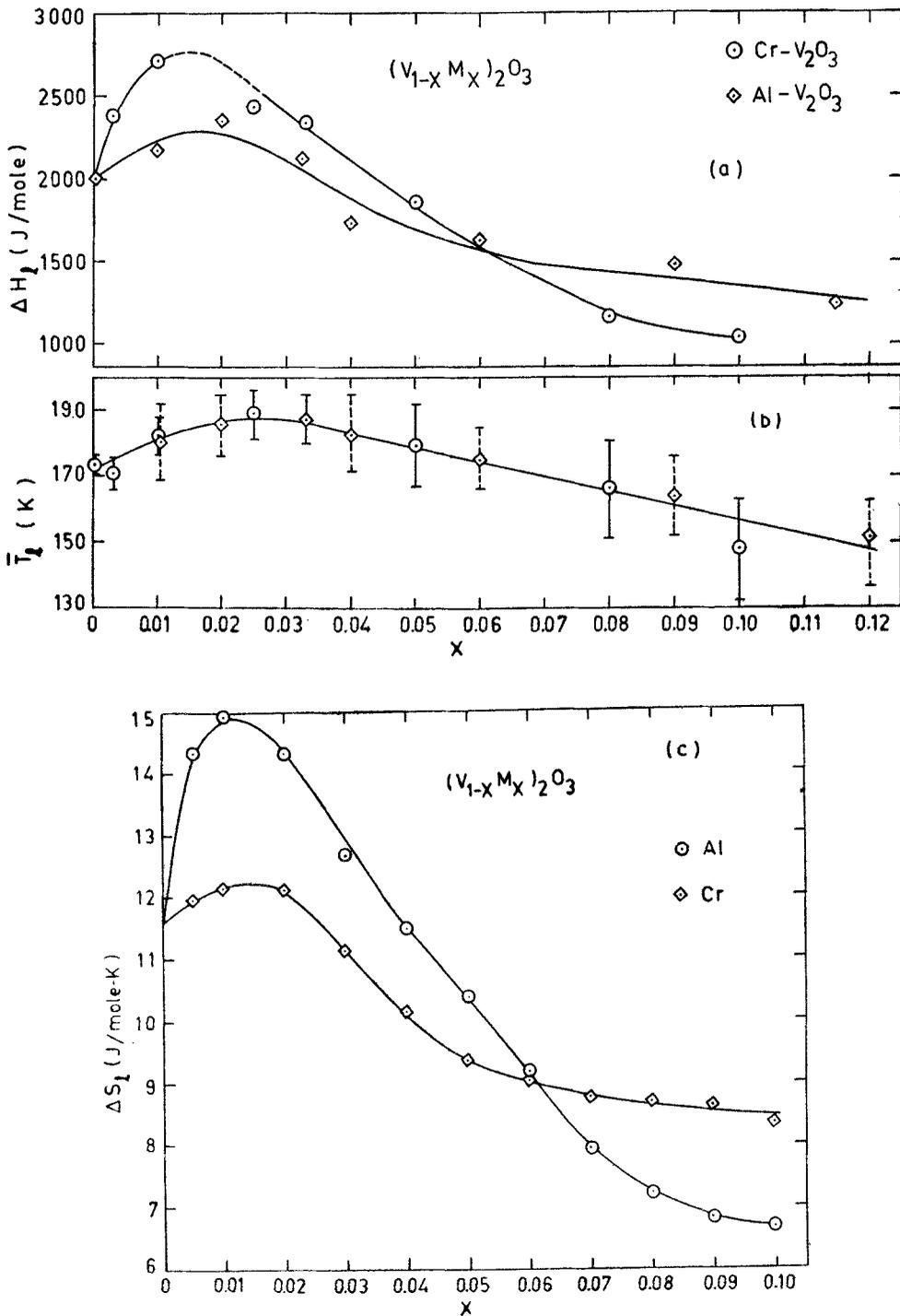
Figure 3. Summary of data obtained for the AFI-M and AFI-I transitions of $(V_{1-x}Cr_x)_2O_3$ and $(V_{1-x}Al_x)_2O_3$ as a function of x. (a) Molar enthalpy change ΔH_l. (b) Average transition temperature, $\overline{T}_l$. (c) Molar entropy change ΔS_l. Numerical values are specified per mole of the $(V_{1-x}M_x)_2O_3$ alloys.

is not greatly influenced by the electronic state of the phase (*i.e.*, whether it is M or I) but rather by the change in magnetic order as one proceeds through the transition.

These concepts may be made more quantitative through the following analysis: It is known (Moon 1970) that the AFI phase is characterized by a magnetic moment of 1·2 Böhr magnetons (μ_B). Since V^{3+} is in the $3d^2$ configuration, it is presumed that only one electron per V atom is involved in the exchange processes that lead to magnetic ordering, and that the second electron participates in strong covalent bond formation which results in the observed V–V pairing and thereby renders this electron magnetically inactive. By contrast, the M and the I phases of groups (II) and (III) respectively are characterized by a value of $p \cong 2\cdot83$ in the relation $\mu = p\mu_B$ for the magnetic moment; thus both the $3d$ electrons per V in the paramagnetic metallic or insulating phases respond to the applied magnetic field. This makes it plausible to assume that there are at least three contributions to the total entropy change ΔS_l at the low temperature (L–T) transition of V_2O_3 or its alloys with Cr_2O_3 and Al_2O_3:
(i) the magnetic disordering effects: $\Delta S_m \equiv (S_p - S_{AFI})_m$, where S_p represents S_M or S_I depending on whether $x < 0\cdot018$ or $x > 0\cdot018$. In zero order approximation $J = 1/2$; then $\Delta S_m = 2R\ln(2J+1)$, which yields $S_p - S_{AFI} = +11\cdot5$ J/mol-K, where the factor of $2R$ accounts for the presence of two V atoms per formula unit.
(ii) In the course of the AFI-M transition ($0 \leqslant x \leqslant 0\cdot018$) the electrons previously participating in covalent bond formation are presumably delocalized. The entropy associated with this process may be calculated according to the Sommerfeld expression $C = \pi^2 k^2 T/2\epsilon_F$ for the electronic heat capacity, along with the standard relation $\epsilon_F = (3\pi^2 n)^{2/3}(\hbar^2/2m)$ for the Fermi level. Then $S_{kin} = \int(C/T)dT$. On assuming a value of the free electron mass for m one computes a value $(S_M - S_{AFI})_{kin} = 0\cdot3$ J/mol-K for the delocalization process. This contribution is absent in the AFI-I transition ($0\cdot018 \leqslant x \leqslant 0\cdot12$) where all bands are essentially filled or empty.
(iii) The contribution of the lattice to the entropy, due to shifts in the phonon mode frequencies at the L–T transition: An estimate of the associated entropy change may be made according to the standard relation for the entropy of a set of lattice vibration frequencies ν_i:

$$S_{ph} = R\sum_i \left\{ x_i/\left[\exp(x_i) - 1\right] - \ln\left[1 - \exp-(x_i)\right] \right\}, \tag{2}$$

where $x_i \equiv (h\nu_i/kT)$; i indexes the various different lattice vibration frequencies. Differentiation of (2) with respect to the frequencies ν_i yields

$$\Delta S_{ph} = -R\sum_i \left(\frac{x_i^2 \exp(x_i)}{[\exp_i(x_i) - 1]^2} \right) (\Delta\nu_i/\nu_i). \tag{3}$$

Values for ν_i, and $\Delta\nu_i$ for the AFI–M or AFI–I transitions have been determined by Fan and co-workers (Kuroda and Fan 1977; Tatsuyama and Fan 1980) for $(V_{1-x}Cr_x)_2O_3$ with $x = 0$, $0\cdot015$, and $0\cdot03$, *via* measurements of Raman scattering. Unfortunately, no comparable infrared reflectivity data or neutron scattering results are available, so that the summation i, in (2) and (3) is necessarily restricted to the seven Raman-active lattice modes. On insertion of appropriate numerical values for T, ν_i and $\Delta\nu_i$, an evaluation of (3) yielded $(S_M - S_{AFI})_{ph} = 1\cdot6$ J/mol-K $(x = 0)$

and 2.1 J/mol–K ($x = 0.015$) as well as $(S_I–S_{AFI})_{ph} = 1.1$ J/mol–K ($x = 0.03$) for the indicated alloy compositions; these numerical values obviously represent approximate values because of the absence of comparable information on the Raman-inactive lattice modes.

On adding the above contributions one predicts entropy changes for the L–T transition of $S_p–S_{AFI} \cong 13.3, 13.9, 12.6$ J/mol–K for $x = 0, 0.015, 0.03$ respectively. Examination of figure 3c shows that the observed $\Delta S_I \equiv S_p–S_{AFI}$ values fall only approximately in line with the calculated quantities. For $x < 0.02$, ΔS lies somewhat above ΔS_{mag}; it therefore seems safe to claim that one of the important mechanisms driving the AFI-M transition is the spin disordering process.

While there is at least a semiquantitative correspondence between calculated and observed values of ΔS_I in the range $0 \leqslant x \leqslant 0.03$, the discrepancies are sufficient to suggest several uncertainties: The assumption that just one electron participates in antiferromagnetic ordering is probably only approximately correct; also, it is impossible to ascertain the total contribution to ΔS_{ph} until information on all lattice modes becomes available in the future. Nevertheless, several unequivocal statements can be made: (i) the total entropy of the metallic phase exceeds that of the antiferromagnetic insulating phase, and (ii) some mechanism must be found which reduces the entropy change associated with the AFI–I transition when x is increased beyond 0.03 for both the Al– and Cr-containing V_2O_3 alloys; for, as is evident from figure 3c, a very significant reduction in ΔS_I occurs at the higher alloy concentrations of Cr_2O_3 or Al_2O_3. In the absence of any information it is impossible to state whether changes in magnetic ordering and/or in lattice modes with alloy concentration are responsible, or whether another entropy-reducing mechanism is involved. (iii) The variation of ΔS_I with x is much more marked for Al than for Cr alloys, since the magnetic properties of the two alloys are virtually identical (Menth *et al* 1971); one must conclude that the differences in the two sets of ΔS_I should be ascribed to significant alterations in lattice properties in switching from Cr to Al as the dopant.

3.2 *High-temperature transition*

A second systematic set of measurements recently completed deals with the enthalpies of transition ΔH_h at the M–I transitions for the Al– and Cr–V_2O_3 alloys in group (II). Some early work had already indicated that ΔH_h values depended on the thermal history and state of subdivision of the samples. In preliminary calorimetric studies Sinha *et al* (1974) encountered a very small enthalpy change $\Delta H_h \approx 100$ J/mol for powdered $(V_{0.99}Cr_{0.01})_2O_3$. In later heat capacity measurements Keer *et al* (1976) reported ΔH_h values in the range 250–330 J/mol for single crystal needles or platelets of $(V_{0.99}Cr_{0.01})_2O_3$ and $(V_{0.99}Al_{0.01})_2O_3$. Clearly, a more detailed investigation is called for.

The measurements cited below were carried out on single crystals of $(V_{1-x}M_x)_2O_3$, with M = Cr, Al grown by the triarc procedure of Fan and Reed (1972). The oxygen stoichiometry was ascertained by reoxidation to V_2O_5 in an atmosphere of oxygen at 670°C. The thermal investigations were done on single crystal needles or platelets cut from boules; a DSC-2 instrument was used with sapphire as a reference standard at a scanning rate of 1.25°/min or 10°/min.

One set of investigations consisted of slow scans across the M-I transition. In confirmation of results reported earlier (Kuwamoto *et al* 1976b) the transition was

manifested by a series of spikes in DSC scans carried out at $1 \cdot 25°/\text{min}$. These spikes vary from one run to the next in number, size, and location on the temperature scale, but they are invariably encountered in every run over exactly the same temperature range in which the $M\text{-}I$ transition is detected electrically as a series of abrupt rises in resistivity. In a few instances only 2-4 spikes were observed, which strongly suggests that for samples of great perfection the transition might occur in a single step.

Several runs were then carried out with fast scans in order to obtain more reliable values of the enthalpy change at the $M\text{-}I$ transition as a function of x in the range $0 \cdot 005 < x < 0 \cdot 018$. These quantities were then converted to entropies of transitions ΔS_h and are displayed in figures 4(a)-(d) for Al- and Cr–doped V_2O_3 in the cooling and heating cycles.

While the scatter in the data is severe, several important points may be established: (i) Consistent with electrical measurements, the calorimetric technique verified that the composition range for the $H\text{-}T$ transition in regime II extended from $x = 0 \cdot 004$ to $x = 0 \cdot 016$ for $Al_2O_3\text{-}V_2O_3$ alloys and from $x = 0 \cdot 005$ to $x = 0 \cdot 018$ for $Cr_2O_3\text{-}V_2O_3$ alloys. (ii) An enormous hysteresis effect is encountered in these transitions; generally, the average temperatures $\overline{T}_h$ for the $M\text{-}I$ transitions in the heating cycles exceeded those in the cooling cycles by 50 to 70 K, even though no large-scale symmetry changes are apparent by conventional x-ray crystallography (McWhan and Remeika 1970; Robinson 1975); however, very slight changes in structure are manifest in meticulous investigations of the phase transformation (Sinclair and Colella 1979). The hysteresis is probably tied to the large volume increase of $1 \cdot 5\%$ when the crystal is converted from the M to the I phase; presumably shrinkage in the cooling cycle can be readily accommodated by the crystal. The increase in volume is brought about by movement of atoms along lines of symmetry in the corundum phase, as detailed in careful studies by Robinson (1975). (iii) The ΔS_h changes at the $M\text{-}I$ transition are positive in the heating cycles and negative in the cooling cycles; thus S_I for the I phase exceeds S_M for the M phase. This is of considerable interest in the context of recent Raman scattering studies on the $(V_{1-x}Cr_x)_2O_3$ system by Tatsuyama and Fan (1980) who report on the basis of their Stokes shifts of Raman active modes that the lattice vibrational frequencies are lower in the M than in the I phase; i.e., for the lattice contributions of Raman active modes to the entropy one finds $(S_M)_{ph} > (S_I)_{ph}$. Therefore, the electronic and other effects must be sufficient to be in conformity with the observation that $\Delta S_h > 0$ or $S_I > S_M$ for the entropy. If the Raman inactive modes contribute in the same manner as the Raman active ones, one concludes that lattice and electronic, acting in opposing directions, jointly control the course of the $M\text{-}I$ transition in these alloys systems. As a first approximation, for $x_{Cr} = 0 \cdot 015$, the entropy difference due to the phonon contributions that can be detected by the Raman studies is $(S_I\text{-}S_M)_{ph} = -1 \cdot 7$ J/mol–K; on this basis, one requires an electronic entropy difference $(S_I\text{-}S_M)_{el} \cong +2 \cdot 9$ J/mol–K (iv) Entropy changes are numerically greater in the cooling as compared to the heating cycles: In part this arises from the fact that the transitions in the heating and cooling modes occur at quite different temperatures. However, the enthalpies themselves are numerically greater in the cooling than in the heating modes. The physical origin for this observation is not clear at this time. (v) The curves depicted in figure 4 exhibit very interesting trends. As x_{Al} is diminished from 0·016 to 0·004, $|\Delta S|$ first rises rapidly to a peak and then falls off gradually toward zero. A similar, though somewhat less pronounced

trend is observed when x_{Cr} is decreased from 0·018 to 0·005. These data indicate that one is headed toward some type of critical point at the lowest value x_{Cr} or x_{Al} at which the *M–I* transition still occurs. These facts are all the more interesting in view of findings by Kuwamoto *et al* (1980), and by Joshi *et al* (1977) that the size of the electrical resistivity discontinuity at the *M–I* transition is essentially independent of x_{Cr} or x_{Al}. In the model proposed by Kuwamoto *et al* (1980), the electron enthalpy change $(\Delta H_M)_{el}$ should be independent of x: the same size gap opens up at the transition, and the same electron population is shifted downward in energy by the same amount for every alloy in regime (II). In this primitive model the electronic contribution to the entropy change $\Delta S_{el} = (S_I - S_M)_{el} = \Delta H_{el}/T_h$ should then vary as T_h^{-1} with the *M–I* transition temperature T_h, as the Cr or Al doping concentration is changed.
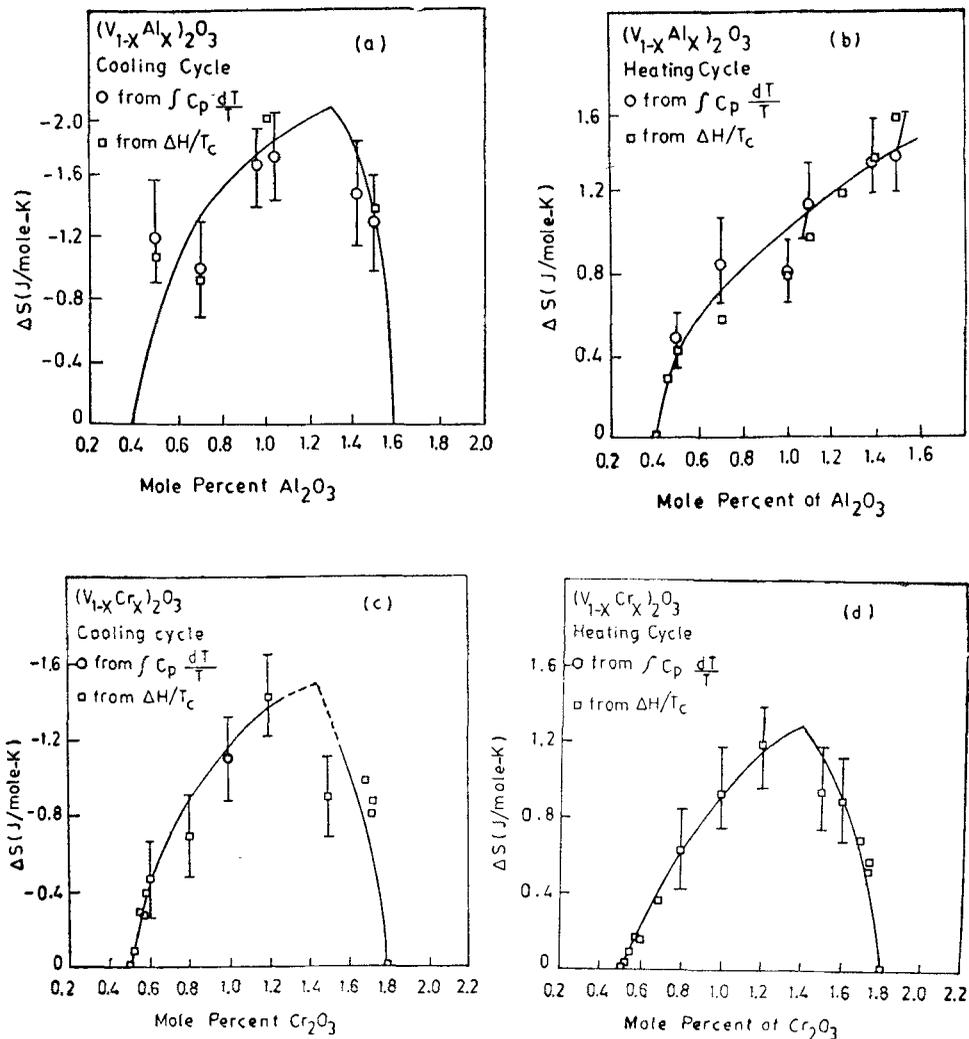

Figure 4. Entropies of transition ΔS for the *M-I* transformation encountered in regime (II). (a) and (b) $(V_{1-x}Al_x)_2O_3$ in cooling and heating cycles. (c) and (d) $(V_{1-x}Cr_x)_2O_3$ in cooling and heating cycles.

A crude estimate of ΔS_{el} is again available by noting the Stokes shifts in the Raman scattering data of Tatsuyama and Fan (1980) on $(V_{1-x} Cr_x)_2O_3$ for $x = 0.015$ and 0.03. This yields directly the change in phonon frequencies for the Raman-active modes at the M-I transition at $T_h = 220K$ and $380K$ respectively. These results were analyzed as described earlier. On insertion of the data into (3) one obtains the result $\Delta S_{ph} \equiv (S_I - S_M)_{ph} = -1.67$ J/mol–K at 220 K and -2.17 J/mol–K at 380 K. These values presumably represent lower limits on $|\Delta S_{ph}|$ for the total vibrational contribution to the entropy change because the Raman inactive modes have been left out of account. Since the observed total entropy changes shown in figure 4 are $\Delta S_h \equiv S_I - S_M = +1.5$ J/mol–K and $= 0$ at 220 and 380 K respectively, therefore $\Delta S_{el} \geqslant +3.2$ J/mol–K and $+2.2$ J/mol–K respectively. These two inequalities satisfy only roughly the criterion that ΔS_{el} should vary as T_h^{-1}. However, the above analysis does lend credence to the hypothesis that the upper critical transition temperature is reached at that value x_0 where the contributions to ΔS_h from the vibrational degrees of freedom of the I vs the M phase balance out of those arising from the differences in electron band structure for the two phases.

4. $(V_{1-x} Ti_x)_2O_3$ and $V_{2(1-y)}O_3$ systems

A systematic study has also been carried out on the enthalpies of transition for $(V_{1-x} Ti_x)_2O_3$ alloys and for nonstoichiometric V_2O_3, undergoing the low temperature AFI–M transition. This permits the thermodynamic characterization of samples belonging to groupings (IV) and (V). The Ti-containing alloys were prepared by arc-melting of appropriate amounts of V_2O_3 and Ti_2O_3 under an atmosphere of gettered Ar, using the triarc technique. Nonstoichiometric V_2O_3 was produced by annealing single crystal V_2O_3 specimens in an appropriate CO/CO_2 atmosphere for 30 hours at 1200°C; the correct stoichiometry was ascertained by reoxidation of sample specimens to V_2O_5 at 670°C. Enthalpies of transition were determined on a specially constructed relaxation calorimeter designed to span the temperature range 30 - 140 K for which no commercial instrument is currently available. The operating principles, constructional details, and characteristics of this device are discussed by Griffing and Shivashankar (1980).

The data are summarized in figure 5; for ease of comparison with the Ti-alloys, the results for nonstoichiometric V_2O_3 are reported in terms of the formula V_2O_{3+x}, wherein $x = 3y/(1-y)$. The dotted extrapolations terminate at a value $x = x_0$ at which T_I is very small; presumably, ΔS_I tends toward zero as well as at that particular x_0. It should be noted that ΔS_I for $x = 0$ as attained in this set of measurements lies roughly 9% below the values for V_2O_3 assembled in table 1. The origin of this discrepancy remains not clear at present; but, as already noted, the lower values are in better agreement with the Clausius-Clapeyron relation, based on the directly measured value of dT/dp (Feinleib and Paul 1967). Therefore, the two values of ΔS_I (for $x = 0.004$ and 0.0055) taken from earlier work (Kuwamoto *et al* 1976a) and entered into figure 5 were adjusted downwards by 9%. These difficulties mentioned here do not detract from the overall results which, despite the scatter of experimental points, show the following trends: (i) as x is increased either for the Ti alloys or with increasing deviations from stoichiometry, the total entropy ΔS_I associated with the $(L$-$T)$ metal-antiferromagnetic insulator transition diminishes drastically, and tends towards zero as $T_I \rightarrow 0$. These findings have important impli-
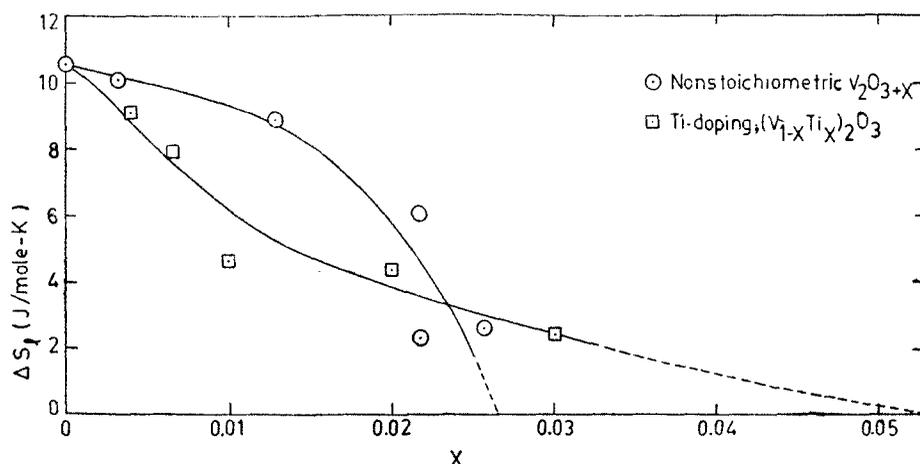
Figure 5. Variation of ΔS_l for the AFI-M transition with x for $(V_{1-x}Ti_x)_2O_3$ and for nonstoichiometric V_2O_{3+x}.

cations: it will be recalled that the observed ΔS_l values in pure V_2O_3 were roughly consistent with values expected for the disordering of magnetic spins in the AFI-M transition. The fact that ΔS_l drops off toward zero on substitution of Ti for V or on incorporation of excess oxygen in the lattice means either that a mechanism is operative which reduces the spin disordering effects with increasing x, or else, that a type of soft mode develops in the lattice which increasingly counteracts the magnetic entropy contribution ΔS_m. These findings call for a very careful follow up study of magnetic ordering in $(V_{1-x}Ti_x)_2O_3$ or in $V_{2(1-y)}O_3$ by neutron diffraction and inelastic scattering techniques, to distinguish between these alternatives; no such data are as yet available. However, there is some indication that magnetic properties are altered on substitution of Ti for V; McWhan and coworkers (1973) found that whereas the magnetic susceptibility χ_M for the metallic phase was almost independent of Ti-doping levels, χ_{AFI} varied strongly with x in a manner suggesting that weaker AFI exchange interactions take place at higher doping levels. (ii) The ΔS_l values for V_2O_{3+x} tend to drop off more slowly at first and then more rapidly with increasing x than do the ΔS_l values for $(V_{1-x}Ti_x)_2O_3$; however, the extrapolated value x_0 at which the M-AFI transition ceases for nonstoichiometric V_2O_3 is almost exactly one-half of the x_0 value for the Ti-containing alloys. This finding is explained on the hypothesis that every excess oxygen ion generates two holes in the lattice, whereas every Ti substitution for V introduces one. This feature strongly supports the DOS model described earlier.

5. Phase diagram for the V_2O_3 system

Using the calorimetric and electrical resistivity studies, it is now possible to set up a phase diagram for the V_2O_3 alloys system. Such information had been compiled by researchers at Bell Laboratories following their initial reports on the properties of the V_2O_3–Cr_2O_3 system (McWhan *et al* 1969; McWhan and Remeika 1970). While this phase diagram is correct in essentials it seems to require modification in the light of the findings des cribed above. The cardinal point at issue is whether or not

the phase boundary separating the *M* and *I* phases on the diagram terminates in a bona fide critical point. It had generally been accepted that this is the case; however, evidence to the contrary is now accumulating.

The revised phase diagram for the $(V_{1-x}Cr_x)_2O_3$ system is depicted in figure 6. The solid lines indicate first-order or near-first-order transitions, and the regions between these represent the observed hysteresis effects. The AFI, M, and I domains are separated from each other as shown on the diagram; the results shown here agree well with those described by the Bell group except for the hysteresis effects which were first described by Rubinstein (1970). We now argue that the region of high temperatures and low *x* values is inhabited by a new metallic, quasimetallic, or degenerate semiconductor phase *M'*, separated from *I* and *M* by second-order or higher-order transitions which extend over a large temperature range of 150 to 200 K. The evidence in support of this hypothesis is two-fold: First, as mentioned earlier, Coey (Coey *et al* 1976; Coey 1977) observed a small enthalpy of transition for pure V_2O_3 undergoing the high-temperature electrical anomaly described for regime (I). Secondly, detailed arguments have been presented elsewhere (Kuwamoto *et al* 1980) and are buttressed by x-ray photoelectron studies (Hegde and Vasudevan 1979) that the gradual reduction of resistivity with rising temperature for alloys in regimes (II) or (III) cannot be understood except on the basis of a shrinking band-gap with rising *T* which ultimately converts the *I* to the *M'* phase. Although no search for thermal anomalies has been made for alloys in groupings (II) and (III),
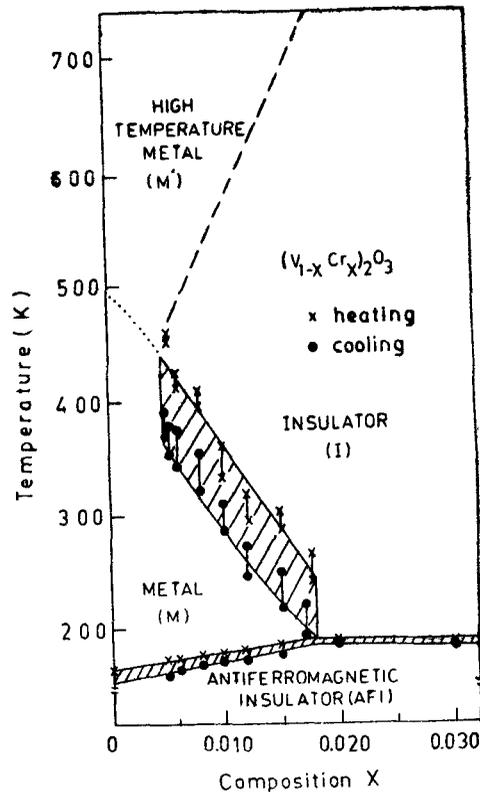

Figure 6. Revised phase diagram for the $(V_{1-x}Cr_x)_2O_3$ alloy system.

it is difficult to avoid the conclusions based on the above measurements that a higher order transition takes place when the *I* phase is heated beyond room temperature.

The occurrence of the proposed *M-M'* and *I-M'* transitions is indicated by dashed lines on the phase diagram; these were arbitrarily drawn to correspond to the temperatures read off from graphs of log ρ vs $1/T$ at the mid-points of the electrical transformations. The precise placement of these lines is immaterial since they are intended solely to map out a wide region on the diagram in which the slow conversion of the *M* or *I* into the *M'* phase is thought to take place.

If these assertions are correct then the termination point of the *M-I* phase boundary is not an ordinary critical point but a singular point at which two higher-order phase boundaries for the *M-M'* and *I-M'* regions meet first order *M-I* phase boundary. The generally accepted idea that the electrical high-temperature anomaly in pure V_2O_3 is simply a supercritical manifestation of the first order *M-I* transition would thus seem to require revision.

Acknowledgement

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