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Spin-spin correlations in the insulating and metallic phases of the Mott system V_2O_3

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Abstract. The magnetic response in V_2O_3 has been investigated using polarised neutron scattering with polarisation analysis. Measurements were carried out at three temperatures corresponding to the antiferromagnetic insulating ground state, the metallic phase and the high temperature metallic phase. At the first order metal insulator transition there is a dramatic change in the magnetic response with the metallic and high temperature metallic phases being characterised by ferromagnetic spatial correlations of the paramagnetic response. The establishment of ferromagnetic correlations at the metal insulator transition accounts for the abrupt jump in the uniform susceptibility. It is proposed that the differentiation of the V-V distances across the edges of VO_6 octahedra is of critical importance for the change in electronic conductivity but also for the establishment of the spatial correlations. The gradual high temperature evolution of the conductivity then occurs by the reduction in the vanadium d overlap brought about by thermal expansion. The first order reduction in atomic volume which occurs on the establishment of the metallic phase results from an instability of the vanadium local moment arising from the change in electronic structure.

PACS. 71.30.+h Metal insulator transitions and other electronic transitions – 75.25.+z Spin arrangements in magnetically ordered materials (including neutron and spin-polarized electron studies, synchrotron-source X-ray scattering, etc.)

1 Introduction

Materials exhibiting metal-insulator (Mott) transitions have received considerable attention ever since Mott suggested the possibility of this many body phenomenon [1]. The materials most extensively studied are various vanadium oxides [2], in particular vanadium sesquioxide V_2O_3 and its alloys with chromium [3]. Below 155 K V_2O_3 is an insulating antiferromagnet. Near 155 K a sharp phase transition to a metallic state [4] without long range magnetic order [5] takes place and around 550 K the material gradually transforms back to an insulating phase [3]. The high temperature transition can be transformed to an abrupt phase transition by doping with Cr [6]. The insulator to metal transition, which occurs at low temperature in stoichiometric V_2O_3, is accompanied by a monoclinic distortion of the trigonal (corundum) structure [5,6]. In spite of considerable experimental and theoretical effort the precise mechanisms giving rise to these phase transitions remain unclear. Broken symmetries invoking magnetic and excitonic order parameters, electron-electron coupling, Peierls transition, charge density waves, strong correlation effects leading to an almost degenerate Fermi liquid and various combinations of these possibilities have been invoked to account for the observed physical properties. According to Mott [7] "there are almost as many theories for this material as there are theorists who have discussed it".

Preliminary polarised neutron scattering experiments [8] indicated that the metallic phase differs dramatically from the low temperature antiferromagnetic phase not only in its electrical properties but also magnetically. The loss of long range antiferromagnetic order does not seem to be caused by the disordering of well defined local moments but instead is due to a substantial change in electronic structure. The paramagnetic scattering observed at large wave vectors Q, appeared too small to be compatible with disordered local moments. Furthermore the observed paramagnetic intensity at large Q was very much lower than the $Q = 0$ value given by the uniform susceptibility. The polarised neutron spectrometer employed did not permit an investigation of the small wave vector response. These observations indicate a strong similarity of the metallic phase in V_2O_3 to itinerant ferromagnets

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above the Curie temperature [9]. In these systems magnetic fluctuations of strong intensity are observed only for small wave vectors and decrease rapidly with increasing Q indicating strong short-range ferromagnetic correlations. Similar dramatic changes in magnetic correlations in a transition from antiferromagnetic insulator to non-magnetic metal have been reported in another vanadium oxide V_5O_9 [10]. Strong changes in the finite energy excitation spectra in V_2O_3 itself were recently reported [11]. On the basis of these results it was proposed that the transition into the antiferromagnetic insulating phase occurred as a result of orbital ordering. The orbital-spin coupling is a non-relativistic effect arising when the superexchange interactions involving partly occupied degenerate orbitals lead to strong coupling between orbital and spin structures. Presented here are the results of a detailed polarised neutron and polarisation analysis investigation of the magnetic fluctuations in V_2O_3. Whilst polarised neutron scattering enables an unambiguous measurement of the paramagnetic response, including the wave vector and frequency dependence it is the absolute magnitude which provides a stringent test of theory. The measurements have been carried out in all three phases namely in the insulating region at 120 K, in the metallic phase at 300 K and finally at 600 K in the high temperature metallic phase.

2 Properties of V_2O_3

At room temperature V_2O_3 is a reasonably good metal with resistivity of the order 10^{-3} Ωcm. When the temperature is decreased below $\sim$ 155 K the compound undergoes a first order phase transition from a metallic to an insulating state, accompanied by an increase in resistivity of $\sim$ seven orders of magnitude [4]. Associated with the transition which exhibits an hysteresis of 10-12 K, is a change in crystal structure [6] from the corundum structure with space group $R\bar{3}c$ to a monoclinic phase with space group I2/a, (a non conventional space group setting of C2/c). A volume expansion of 3.5% occurs on cooling through the transition [12]. In the low temperature phase the system orders antiferromagnetically with the V moments coupled ferromagnetically in the monoclinic (010) layers, originating from the (110) hexagonal planes, with adjacent planes coupled antiferromagnetically [5]. Thus the monoclinic distortion in the low temperature phase is believed to be magnetostrictive in origin. There are four and six vanadium atoms in the monoclinic and the rhombohedral cell respectively, with each vanadium atom contributing two $3d$ electrons. For trigonal symmetry the five orbital d functions split into an a_1 function and two doubly degenerate e_g functions. The antiferromagnetically ordered moment per vanadium atom was determined to be $1.2\mu_B$, much less than the $2\mu_B$ expected for two $3d$ electrons on V^{3+}, and has been attributed [13,14] to a contribution of $1\mu_B$ from "localised" electrons of a_1 symmetry and $0.2\mu_B$ from "itinerant" e_g electrons. Interpretation of heat capacity measurements have lead to the conclusion that the metallic phase is characterised by a large electronic contribution 54.6 $\mathrm{mJK^{-2}mol^{-1}V}$ [15]. In the metallic phase the magnetic susceptibility is anomalously high but drops abruptly by a factor of nearly 2 at the transition [16,17]. NMR [18] and susceptibility measurements have been combined to separate the contributions to the measured susceptibility in the metallic phase into temperature independent diamagnetic (dia) and van Vleck (vv) parts and a temperature dependent $3d$ part obeying a Curie-Weiss law

$$\chi(T) = \chi_{\mathrm{d}} + \chi_{\mathrm{vv}} + \chi_{\mathrm{dia}} \tag{1}$$

with

$$\chi_{\mathrm{d}}(T) = \frac{C}{T-\theta} \tag{2}$$

with $C = 0.657$ emu mole^{-1}K and $\theta = -600$ K giving $\mu_{\mathrm{eff}} = 2.37\mu_B$ per vanadium atom. However over the temperature range for which the Curie-Weiss behaviour is reported [17], namely 155 to 300 K, the observed susceptibility only falls by 20%. Between 300 and $\sim$ 550 K the susceptibility is only weakly dependent on temperature. Above $\sim$ 550 K the observed susceptibility has been analysed to yield a Curie-Weiss behaviour with $\theta = -600$ K and $\mu_{\mathrm{eff}} = 2.69\mu_B$ per vanadium atom. However this analysis is valid only if χ_{vv} takes the value 0.21 μemu/mol, which corresponds to the value of χ_{vv} calculated for vanadium [19]. The calculated spin only values of μ_{eff} for V^{3+} and V^{4+} are $2.83\mu_B$ and $3.87\mu_B$ per vanadium atom respectively. Associated with the essentially temperature independent susceptibility between 300 and $\sim$ 600 K is an anomalous change in conductivity to a metallic state above $\sim$ 600 K [20]. Both phases of this high temperature transition appear to have the corundum structure but with an increase in the c/a ratio as the temperature rises [21]. The metallic phase can be stabilised at all temperatures by alloying with Ti_2O_3, [22–24] varying the oxygen stoichiometry [25–27] or by hydrostatic pressure [28,29]. For small concentrations of vanadium vacancies ($V_{2-x}O_3$ with $0.018 \le x \le 0.035$) an incommensurate spin density wave has been identified below $T_N \sim 12$ K yielding an ordered moment of $0.15\mu_B$ per vanadium atom [30].

3 Experimental

A V_2O_3 powder sample (Johnson Matthey) was checked by X-ray diffraction at room temperature and found to be single phase. It has the corundum structure, space group $R\bar{3}c$, with cell parameters $a = 4.947\,5(7)$ Å and $c = 14.004(7)$ Å, in good agreement with earlier reported data [31,6] for the stoichiometric compound. Susceptibility measurements carried out using a SQUID magnetometer over the temperature range 4 to 300 K, revealed an anomaly at $\sim$ 155 K in agreement with earlier measurements [16,17]. An anomaly at this temperature was also observed in the electrical resistivity from measurements made on a compacted pellet.

Measurement of the paramagnetic response as a function of wave vector was carried out using the polarised neutron spectrometer D7 at the ILL Grenoble. The incident neutron wavelength of 4.84 Å and the 32 detectors enabled simultaneous measurement of the response over the wave vector range $0.1 < Q < 2.5$ Å^{-1}. Polarisation of the incident beam and analysis of the scattered beam, by each of the 32 detectors, was made using polarising supermirrors. A coil placed in the incident beam before the sample allowed the neutron spin to be reversed. Three mutually perpendicular Helmholtz coils around the specimen position enabled the incident neutron spin to be rotated along the axis of the three coils. The efficiency of the 32 detectors was determined using the scattering from a standard vanadium specimen. A quartz glass sample was used to determine the polarisation efficiency of each detector/mirror arrangement. The average flipping ratio of the 32 detector systems was found to be 30 ± 1.5. For measurements at 120 K and 300 K the 20 g powder sample was contained in a thin walled aluminium tube located in a helium flow cryostat. A non-inductively wound furnace was used for the high temperature measurements at 600 K. The scattering from the sample was placed on an absolute scale using the vanadium normalisation. This procedure was verified using the nuclear spin incoherent scattering from the sample, which is expected to arise entirely from the presence of vanadium. The observed differential cross section was 0.84 ± 0.02 barns/str/atm which compares favourably with the reported value for vanadium of 0.826 barns/str/atm [32].

An unambiguous separation of the paramagnetic scattering from all other contributions was made using the XYZ method [33] and the vector nature of the magnetisation-neutron interaction. Only the magnetic component is dependent on the relative orientation of the scattering vector, so by measuring the spin flip (SF) and non spin flip (NSF) scattering associated with the X, Y and Z directions the magnetic contribution can be extracted by subtracting the following partial cross sections

$$\langle \mathrm{d}\sigma_{\text{para}} \rangle = \langle \mathrm{d}\sigma_x^{\text{NSF}} \rangle + \langle \mathrm{d}\sigma_y^{\text{NSF}} \rangle - 2\langle \mathrm{d}\sigma_z^{\text{NSF}} \rangle \qquad (3)$$

and

$$\langle \mathrm{d}\sigma_{\text{para}} \rangle = -\langle \mathrm{d}\sigma_x^{\text{SF}} \rangle - \langle \mathrm{d}\sigma_y^{\text{SF}} \rangle + 2\langle \mathrm{d}\sigma_z^{\text{SF}} \rangle \qquad (4)$$

where the z axis is taken to be vertical.

The paramagnetic component can be obtained from either the spin flip or the non spin flip scattering. Usually the spin flip channel is used to extract the magnetic scattering since it contains fewer contributions, essentially only the magnetic and nuclear spin incoherent components. Vanadium has a large nuclear spin incoherent scattering which is wave vector independent but necessitates data of good statistical significance in order to obtain the paramagnetic component from the spin flip channel.

The polarised neutron technique not only enables the isothermal determination of the magnetic cross section but also its spatial and temporal dependence. If the scattering is placed on an absolute scale then the measurements provide a powerful test of theory. The experiment on V_2O_3 was concerned only with the wave vector dependence of the magnetic response, with the scattering integrated over an energy range up to ~ 30 meV. If relativistic effects are unimportant and spin is conserved the observed scattering will extrapolate to the cross section at $Q = 0$ given by the uniform susceptibility χ. The spin-spin correlation function $\langle \mathbf{S}_q \cdot \mathbf{S}_{-q} \rangle$ at $Q = 0$ is given by $\sum_j \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = 3\chi k_{\text{B}} T$ which is related to the partial differential cross section by $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_j \frac{2}{3} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \left(r_{\text{o}}\gamma\right)^2 f^2$ where $(r_{\text{o}}\gamma) = -0.54 \times 10^{-12}$ cm and f is the form factor which is unity at $Q = 0$.

The magnetic correlation function

$$S(\mathbf{q}, \omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t} \sum_{i,j} \mathrm{e}^{\mathrm{i}\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} \langle \mathbf{S}_i(t) \cdot \mathbf{S}_j(0) \rangle \qquad (5)$$

is related to the imaginary part of the dynamic susceptibility

$$S(\mathbf{q}, \omega) = \frac{1}{1 - \mathrm{e}^{-\frac{\hbar\omega}{kT}}} \chi''(\mathbf{q}, \omega) \cdot \qquad (6)$$

A sum rule for the scattering can then be defined

$$\sum_{\mathbf{q}} \int_{-\infty}^{\infty} \mathrm{d}\omega S(\mathbf{q}, \omega) = \int_{-\infty}^{\infty} \mathrm{d}\omega \sum_{\mathbf{q}} \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t} \sum_{i,j} \mathrm{e}^{\mathrm{i}\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} \langle \mathbf{S}_i(t) \cdot \mathbf{S}_j(0) \rangle \qquad (7)$$

which yields

$$N\langle S^2 \rangle = NS(S+1). \qquad (8)$$

In the ordered ground state the Bragg peaks contribute $(bS)^2$ and the spin waves $(1 - b^2)S^2 + S$ (where b is the reduction factor due to longitudinal fluctuations). Thus in order to obtain the sum rule it is necessary to integrate up to the maximum spin wave energy. For some systems this may not be experimentally feasible, but the technique described above which places the scattering onto an absolute scale enables a precise comparison with model calculations of the wave vector and energy dependence of the response. For local moment systems well above the ordering temperature T_{N} the correlation $\langle \mathbf{S}_I \cdot \mathbf{S}_I \rangle = S(S+1)$ and the sum rule is recovered. Again the integration has to be over the same energy range which is typically equal to $k_{\text{B}}T_{\text{N}}$. However in the paramagnetic phase the response is quasi-elastic with the magnetic weight peaked at zero energy. However local magnetic moments are meaningful variables only if the magnetic excitation spectrum ω_{mag} and charge excitation spectrum ω_{ch} are separated, namely $\omega_{\text{mag}} \ll \omega_{\text{ch}}$. This situation is usually satisfied for ionic magnets such as MnF_2 in which the Coulomb forces giving rise to Hund's rule moments are much stronger than the thermal energies kT_{N} characterising magnetic fluctuations [9].

For metallic systems the spectra of charge and spin fluctuations overlap and the concept of a local moment is not well defined. An average magnetic moment can be obtained in the magnetically ordered phase from Bragg scattering which is a $q = 0$ and $\omega = 0$ measurement. However it is not possible to establish a sum rule based on this value. The dynamic response is characterised by the band motion of the electrons which is determined by the bandwidth. A sum rule does exist based on the occupation of the band and integration over the Brillouin zone up to the bandwidth. However a reliable separation of the thermal and quantum fluctuations is not generally possible, particularly if there is a change in electronic structure from the ground state [9].

4 Results

The spin flip scattering observed (Fig. 1) in the low temperature insulating phase at 120 K was consistent with that reported by Moon [5]. Within the wavevector range studied the (001), (010) and (−201) antiferromagnetic Bragg peaks were clearly resolved. The intensity of these peaks are consistent with the proposed antiferromagnetic structure in which the vanadium moments of $1.2\mu_\mathrm{B}$ are ferromagnetically coupled in (110) planes of the hexagonal lattice with adjacent planes coupled antiferromagnetically. The uniform background observed below ~ 1 Å^{-1} corresponds to a cross section of 0.0075 b./str/fu.

On raising the temperature above 155 K the form of the magnetic scattering significantly altered with the sharp antiferromagnetic peaks disappearing as expected. The wave vector dependence of the paramagnetic scattering observed at 300 (Fig. 2) and 600 K (Fig. 3) was similar, with the main feature being the enhancement of the scattering at small wave vectors and around strong nuclear Bragg peaks. Such behaviour is expected if there exist spatial correlations of the magnetisation density which are ferromagnetic in nature. Unpolarised neutron scattering carried out at 200 K on a single crystal specimen also reported the presence of ferromagnetic correlations [11]. Measurements carried out around the position of the antiferromagnetic wavevectors did not reveal any significant enhanced scattering. The two temperatures at which measurements were made in the paramagnetic phase, namely 300 and 600 K correspond approximately to twice and four times the transition temperature at which the paramagnetic state occurs. Experimental constraints did not permit measurements to be made below ~ 0.2 Å^{-1} and therefore obtain a precise determination of the correlation length. An "estimate" was obtained using the value of the cross section at $Q = 0$ as given by the uniform susceptibility and assuming an Ornstein-Zernicke dependence. This analysis indicated that the range of correlation 6–9 Å did not effectively change between 300 and 600 K. The value of the correlation length obtained in this way is similar to that observed in V_5O_9 [10]. The total amount of scattering per vanadium atom was obtained by integrating the observed scattering up to a wave vector determined by the atomic volume Ω namely $Q_0 = \left(\frac{6\pi^2}{\Omega}\right)^{1/3}$

$$\langle \mathbf{M}_i \cdot \mathbf{M}_i \rangle = \left[\frac{\Omega}{2\pi^2}\right] \int_0^{Q_0} \langle \mathbf{M}_{-q} \cdot \mathbf{M}_q \rangle \mathrm{d}Q. \tag{9}$$

This yielded an amplitude per vanadium atom of $0.35(1)\mu_\mathrm{B}$, $0.35(1)\mu_\mathrm{B}$ and $0.5(1)\mu_\mathrm{B}$ at 120, 300 and 600 K respectively. The value obtained at 120 K did not include the magnetic Bragg scattering, only the magnetic diffuse scattering. As already discussed, these values should not be interpreted as atomic moments. The energy integration has not been carried out over the appropriate bandwidth but over the corresponding thermal energy range. However the loss of long range magnetic order does not give rise to an increase in the magnetic diffuse scattering as would be expected for thermally disordered local moments of $1.2\mu_\mathrm{B}$. The amplitude observed at 290 K is smaller than the $0.61\mu_\mathrm{B}$ reported for V_5O_9 obtained using similar experimental conditions [10]. A value of $0.5(1)\mu_\mathrm{B}$ per vanadium atom was obtained for V_2O_3 in earlier polarised neutron experiments [8] using high energy neutrons which enabled an energy integration over twice the thermal energy range.

5 Discussion

The thermal variation of the uniform susceptibility is complex but has been analysed to reveal Curie-Weiss behaviour over discrete regions namely 155 to 300 K and above 600 K [17]. The values of the effective moment in each regime are different and inconsistent with the theoretical values expected for V^{3+} or V^{4+} and with the value estimated from the observed ground state moment. Furthermore the paramagnetic Curie temperature derived for each regime, namely −600 K is high. In the metallic phase similar behaviour is observed for systems in which the Fermi level falls close to a peak in the density of states. Castellani *et al.* [34] have proposed that the susceptibility in the metallic phase is characteristic of a narrow band Stoner enhanced Pauli paramagnet. In the non interacting limit the susceptibility and Sommerfeld coefficient of the specific heat are related to the bare density of states by

$$\frac{\chi}{13.71} = \frac{\gamma}{0.212} = N(\varepsilon_\mathrm{F}) \tag{10}$$

where χ is in μemu/mol, γ is in mJ/(mol K^2) and $N(\varepsilon_\mathrm{F})$ is given by states/eV atom. The magnitude of both the susceptibility $\chi = 10^3$ μemu/mol and the Sommerfeld coefficient $\gamma = 54.6$ mJ/(mol K^2) in the metallic phase are anomalously large producing a value for the density of states $N(\varepsilon_\mathrm{F})$ substantially greater than that calculated. The value for γ was obtained by suppressing the transition temperature and extending the metallic phase to lower temperatures by either changing the stoichiometry [27] or by the application of pressure [26]. Thus care must be

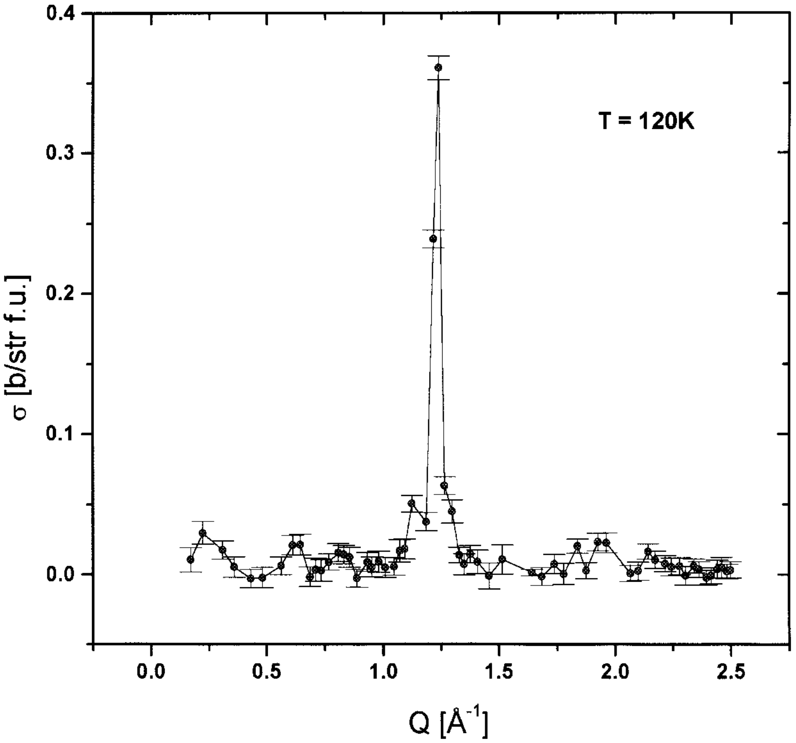


Fig. 1. Spin flip scattering in the low temperature insulating phase of V_2O_3 at 120 K.

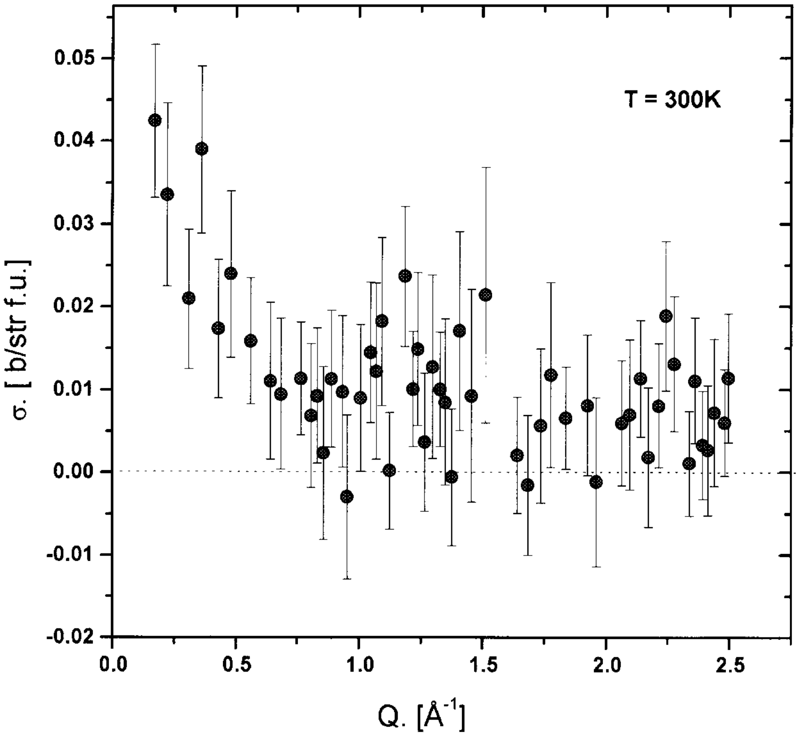


Fig. 2. Paramagnetic scattering in the metallic phase of V_2O_3 at 300 K.

taken in attributing the γ values derived in this way to the metallic state of pure V_2O_3 at ambient pressure. Recent specific heat measurements [26,27] indicate that the metallic state of V_2O_3 looks quite different as a function of band filling (change in stoichiometry) or of pressure. Under pressure the derived γ values are reported to increase while as a function of band filling they decrease. Furthermore the analysis and the band structure calculations do not include many body effects such as electron-electron and electron phonon interactions which influence χ and γ. McWhan [15] has pointed out for such systems that $\chi/\gamma \ll 1$ implies strong electron-phonon interaction,

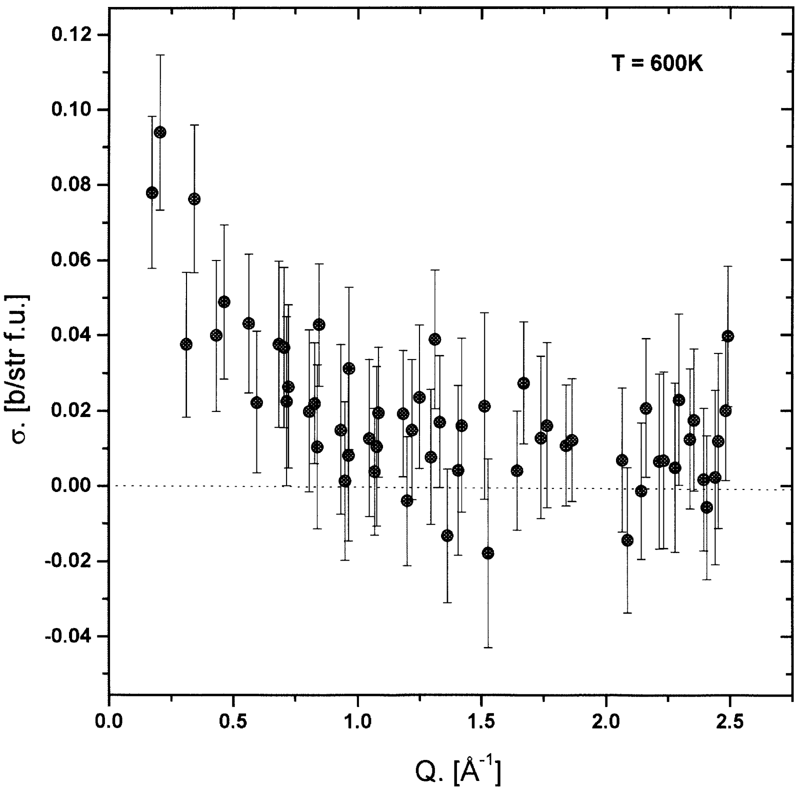


Fig. 3. Paramagnetic scattering in the high temperature metallic phase of V_2O_3 at 600 K.

$\chi/\gamma \approx 1$ implies spin fluctuations and $\chi/\gamma \gg$ implies paramagnons, and on the basis of the analysis it was concluded that spin fluctuations dominate in V_2O_3.

The concept of local moments in which the electrons giving rise to the magnetism participate in the transport properties and the use of a Curie-Weiss model is highly questionable. Indeed low temperature NMR measurements carried out under pressure indicate the absence of local moments [35]. Significant thermal variation of the uniform susceptibility at temperatures well below that corresponding to the Fermi temperature is observed in many strongly correlated magnets such as MnSi, $ZrZn_2$, Ni, Fe, etc. [36]. In these materials neutron measurements have shown that the paramagnetic state is characterised by spin fluctuations which can persist up to many times the ordering temperature [9]. It is the presence of the spatial correlations in V_2O_3 and the underlying mechanism that is the key to understanding the metal insulator transition.

The magnetic moment per vanadium atom obtained at 77 K in the antiferromagnetic phase is significantly smaller than the $2\mu_B$ expected for a V^{3+} ion. Several possibilities for this behaviour have been proposed including, itinerancy of the $3d$ electrons (covalency) [34], a crystal field model in which an isolated V^{3+} ion in an octahedral field has opposing spin and orbital moments [18] and a band model in which one of the two $3d$ electrons is completely polarised and the other only partially [13,14]. Recent polarised neutron measurements [37] of the spatial distribution of the magnetisation density induced at 180 K by a field of 4.6 T support the model proposed by Castellani. The results show that the moment on the vanadium atoms is almost entirely due to electrons in the doubly degenerate orbitals which are supposed to give rise to orbital ordering. Significant negative moment amounting to some 6% of the total was found on the oxygen sites which could only occur due to covalency.

The thermal variation of the moment in the antiferromagnetic phase would suggest a transition to a paramagnetic state around 300 K [5], well above the first order phase transition at 155 K where long range magnetic order in fact disappears. However the disappearance of long range magnetic order at 155 K is not the result of thermal disorder of local moments of fixed amplitude. In general for local moment systems the magnetic ordering temperature T_N is typically of the same order of magnitude as the zone boundary spin wave frequency observed in the ground state. The magnon dispersion in V_2O_3 has been partially determined up to $\sim$ 25 meV [38]. The results reveal an anisotropy gap of 4.75 meV and anisotropic dispersion consistent with the antiferromagnetic coupling being much stronger than that between parallel spins. The zone boundary energy for modes propagating along the (001) direction is approximately 25 meV which is of the same order as the extrapolated Néel temperature. However the substantial change in electronic structure at the transition renders any description of the metallic phase based on the ground state highly speculative.

At the metal-insulator transition there is a significant change in crystal structure involving $\sim$ 3.5% reduction in the volume of the lattice in the metallic phase, with the vanadium-vanadium distances becoming shorter and less

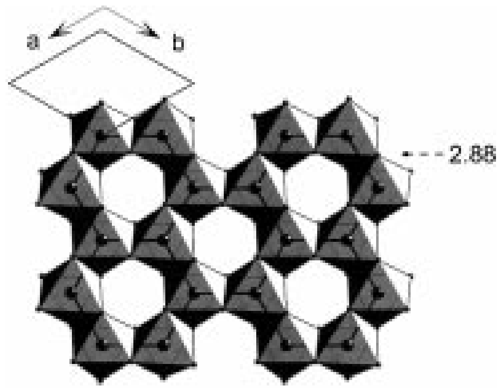


Fig. 4. Projection along the *c* axis of a single layer of VO_6 octahedra in the high-*T* structure of V_2O_3 (rhombohedral R-3c, unit cell outlined, distances V-V = 2.88 Å shown).

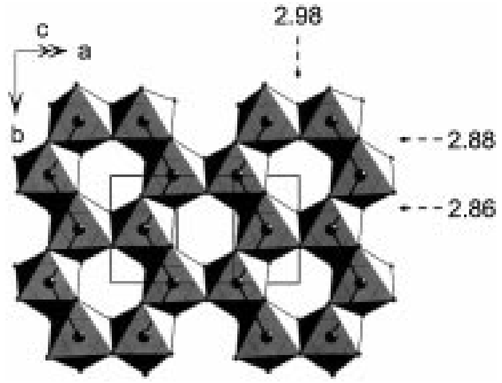
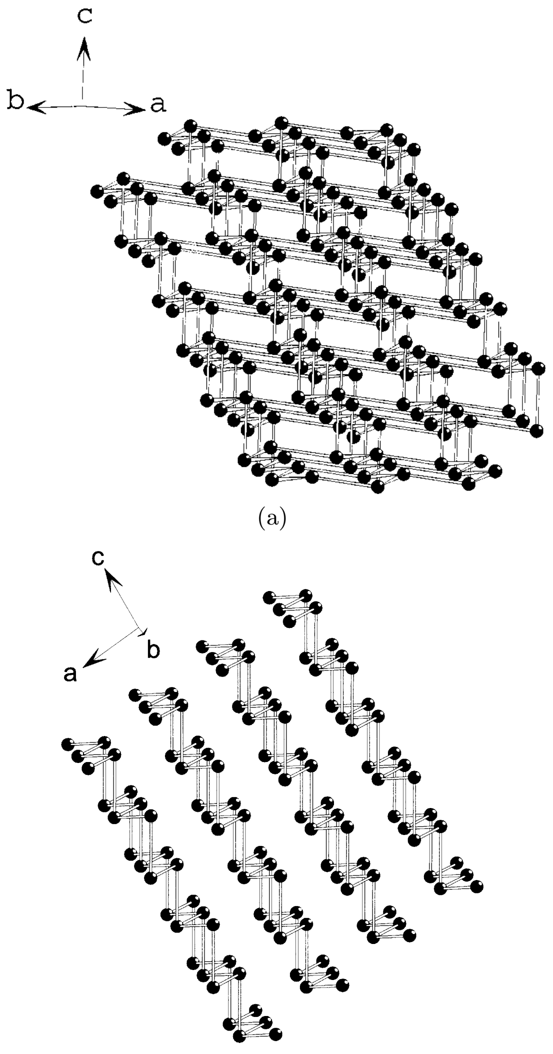


Fig. 5. Projection of a layer in an appropriate direction of the low-*T* structure (monoclinic I2/a, differentiated V-V contacts indicated).



(a)

(b)

Fig. 6. Patterns of close V-V contacts in (a) High-*T*-V_2O_3 (3D-framework of short V-V distances) and (b) low-*T*-V_2O_3 (2D-array of short V-V distances). The vertical lines correspond to shortest V-V distances, 2.70 and 2.75 Å, respectively (see text).

differentiated and the vanadium-oxygen distances remaining essentially unchanged. The structure of V_2O_3 at ambient temperatures (corundum type) is formed from layers orthogonal to the *c* axis, one of them being depicted in Figure 4. Such layers of hexagons of edge sharing VO_6 octahedra have a composition $VO_{6/2} = VO_3$. The 3D structure results from successive shifts of identical layers by 1/3 along the (long) cell diagonal with the consequence that the O atoms between adjacent layers are shared according to $VO_{3/2}$ corresponding to V_2O_3. This stacking has the consequence that half of the octahedra share faces with octahedra in the upper and half with those in the lower layer resulting in V-V dumbbells with the short distance of 2.70 Å whereas the V-V distances within the layers (contacts across octahedron edges) are 2.88 Å. The short distance is at first hand a trivial consequence of face sharing of the octahedra.

The crystallographic transformation to the low temperature structure [5,6] becomes most obvious by depicting the corresponding projection of the layers which now are distorted with V-V distances ranging from 2.86 to 2.98 Å (see Fig. 5). The V-V distances between adjacent layers (across octahedral faces) have increased to 2.75 Å. In addition to the increase of the inter-layer V-V distances the other change which takes place through the phase transition pertains to the intra-layer V-V distances. These develop into a quasi 1-D pattern of zig-zag chains of V atoms with only a small differentiation of the V-V distances (2.86 *vs.* 2.88 Å) in the chains. Taking into account the short inter-layer V-V distances the monoclinic distortion breaks the 3-D metal-metal bonding framework into 2-D nets as shown in Figure 6.

The occurrence of magnetic moments in metallic magnets depends on correlation effects and the band width which is essentially determined by the nearest neighbour metal-metal distance. In the case of vanadium this has been extensively studied in compounds such as Au_4V [39]. The absence of nearest neighbour V-V interactions is believed to be important for the formation of local vanadium moments. Theoretically the volume dependence of the magnetic moment in bcc vanadium has been studied by Hattox *et al.* [40] who found that a local moment is formed for V-V distances given by 2.85 Å $< d_{\mathrm{V-V}} <$ 3.8 Å.

Subsequent LSDF calculations [41] reveal three critical distances corresponding to a non magnetic, a low spin and to a high spin state. The loss of magnetic order observed in V_2O_3 is not dissimilar to the behaviour found in YMn_2 where a paramagnetic state is established at a first order phase transition involving a $\sim 5\%$ reduction in cell [42] volume. This behaviour is associated with a collapse of the local Mn moment. However it may be noted that the level of scattering in V_2O_3 towards the zone boundary *e.g.* between ~ 0.6 and 1 Å^{-1} does not effectively increase on warming to 290 K as would be expected on the loss of long range magnetic order corresponding to a moment of (gS) *i.e.* $1.2\mu_{\mathrm{B}}$. Although the paramagnetic state of YMn_2 is characterised by well defined spin fluctuations, [43] these occur around the staggered wave vector. In V_2O_3 the spin fluctuations are of a ferromagnetic nature and are clearly responsible for the jump in susceptibility at the first order phase transition. Since V_2O_3 orders antiferromagnetically fluctuations may be expected around the staggered wave vector particularly close to the Néel temperature. However, as the transition at 155 K is not a true magnetic phase transition, being of first order, thermodynamic fluctuations should not be important. Clearly the ferromagnetic correlations persist beyond 600 K and are not simply residual short range order but arise from a fundamental change in the wave function. At the phase transition there is a change by seven orders of magnitude in the electrical conductivity reflecting the increased overlap of the d functions. Thus whilst antiferromagnetic coupling dominates the ferromagnetic exchange below 155 K this could alter when the mechanism changes with the introduction of a conduction band. Whilst the ground state magnetic structure comprises of ferromagnetically coupled spins in the (110) planes it is not possible on the basis of the present powder measurements to state whether it is the same spins which are correlated in the paramagnetic phase.

Fundamental to understanding the metal insulator transition is a precise knowledge of the electronic states involved and identification of the important correlation effects. As early as (1960) Goodenough [44] stressed the importance of direct V-V interactions in V_2O_3. Covalent bonding of $a_{1\mathrm{g}}$ electrons between pairs of vanadium atoms along the direction $[001]_{\mathrm{h}}$ is predicted to give rise to the high temperature non co-operative cross over transition [44]. The weaker V-V interactions in the basal plane are then thought to produce the low temperature first order transition. Subsequently Castellani *et al.* [34] proposed that the magnetic properties of the metallic phase could be described by a $3d$ band model of e_{g} symmetry with a highly enhanced Stoner susceptibility. The spin fluctuations producing the enhancement being mainly confined to V-V pairs along the c axis. The importance of the V-V pairs was also emphasised in the excitonic model proposed by Ashkenazi and Weger [13]. Recent band structure calculations [45] indicate that the partially filled bands at the Fermi surface involve all five $a_{1\mathrm{g}}$ and e_{g} states. However the induced magnetisation density at 180 K was observed to have e_{g} anisotropy [37].

Further insight into the importance of the V-V nearest neighbour distance can be obtained with reference to the phase diagram of V_2O_3 as a function of metal doping. Doping with Ti $(\mathrm{Ti}_x\mathrm{V}_{1-x})\mathrm{O}_3$ suppresses the antiferromagnetism and establishes the metallic phase for $x > 0.055$ down to lowest temperatures. A similar result also occurs in the V_2O_{3+x} system for $x > 0.03$. However the effects of Cr doping are quite different primarily affecting the properties above the antiferromagnetic insulating state. The first order onset of antiferromagnetism is observed in all systems that undergo a metal insulator transition. Associated with the first order transition is a change of atomic volume. Of all the transition metal sesquioxides with the corundum structure, the metallic conductivity and high c/a ratio makes V_2O_3 unique. Whilst doping with Ti or Cr affect the phase diagram differently, they both reduce the c/a ratio. However, unusually the nearest neighbour distance is not reduced in both systems. A one percent substitution of Cr^{3+} in V_2O_3 causes a drop in c/a from 2.83 to 2.78 whilst the resistivity increases by several orders of magnitude. A remarkable feature is that the nearest neighbour vanadium distance increases. For $(\mathrm{V}_{0.962}\mathrm{Cr}_{0.038})\mathrm{O}_3$ the distance increases from 2.697 in V_2O_3 to 2.746 Å despite the contraction of c from 14.003 Å to 13.912 Å. The V-V distance in $(\mathrm{V}_{0.962}\mathrm{Cr}_{0.038})\mathrm{O}_3$ is very close to that of 2.74 Å observed in the antiferromagnetic monoclinic phase of pure V_2O_3. In addition the interatomic vanadium-vanadium distance across the shared octahedral edge increases by approximately 1.2% which compares well with the observed 1% expansion in a. In the case of Ti doping the c parameter and the V-V nearest neighbour distance along the c axis decrease to 2.59 Å and 13.7 Å respectively. In the absence of detailed crystallographic information of the $(\mathrm{Ti}_x\mathrm{V}_{1-x})\mathrm{O}_3$ system and assuming a linear variation of the nearest neighbour V-V distances then antiferromagnetism disappears at a value of 2.737 Å.

6 Conclusion

The paramagnetic phase of V_2O_3, including both metallic regimes is characterised by a ferromagnetically correlated spin density similar to that observed in the paramagnetic phase of transition metal ferromagnets [9]. The long wavelength thermal spin fluctuations are enhanced whereas those of short wavelength overlap with quantum fluctuations and give rise to a low level of scattering in the thermal region. The onset of ferromagnetic correlations at the metal-insulator transition accounts for the abrupt jump in the uniform susceptibility. Associated with this transition is the loss of long range magnetic order. However the transition which is of first order is not a true Néel temperature but arises from a substantial change in the crystallographic and electronic structure. The reduction in atomic volume which also occurs on the establishment of the metallic state arises from an instability in the local vanadium moment. The present result clearly indicates a substantial reduction in the paramagnetic moment within the thermal energy range. A similar observation is obtained for NiS [46] which also undergoes a metal insulator transition with a change in atomic volume and a collapse of long range magnetic order. Whilst similarities exist between the volume collapse and moment instability detailed differences in the paramagnetic response are to be expected owing to differences in crystallographic structure and electronic configuration of the metal atoms. Vanadium which is at the beginning of the $3d$ series will have a more extended wave function, and indeed direct V-V interactions along the c direction are reported to influence the physical properties of V_2O_3. It is probable that the ferromagnetic correlations in the paramagnetic phase are a manifestation of these V-V interactions. The absence of substantial thermal variation of the correlations clearly indicates that their origin is not one of residual short range order arising from thermal fluctuations close to the transition temperature but arise from details of the electronic structure. Further measurements extending to lower wave vectors are required to quantify the range of correlations. However there are no polarised neutron spectrometers presently available on which to carry out such investigations.

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