Interplay of orbital ordering and exchange interaction in V_2O_3

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Abstract

Orbital ordering in V_2O_3 appears due to the orbital degeneracy of the doubly degenerate ground state of the V^{3+} ions and causes an antiferromagnetic phase transition in this compound. Assuming a crystal field of symmetry lower than cubic and spin–orbit coupling, the magnetic properties of this compound have been studied. Correlated effective-field theory is used to study the magnetic properties of the insulating phase. The magnetic structure observed at low temperature is also incorporated in the calculation.

1. Introduction

The transition metal oxides are important as regards their magnetic as well as their transport properties. These oxides are Mott insulators in which an insulating-to-metallic transition can be induced by changes in temperature and pressure, alloying and nonstoichiometry. V_2O_3 is one such compound which exhibits an antiferromagnetic-to-paramagnetic transition in the insulating phase. The V_2O_3 system is now a topic of much interest because of its rich phase diagram, although both theorists and experimentalists have been engaged in the investigation of the transport and magnetic properties of this compound for a long time. Recently there has been renewed interest in this compound due to the discovery of high-T_c phenomena in Cu-based transition metal oxides. Recent [1, 2] studies, however, led to a new concept and earlier theories may not give the correct picture [1] of V_2O_3. The antiferromagnetic ordering [3] in the insulating phase suggests orbital ordering in the doubly degenerate E_g orbitals consistent with neutron scattering results [4]. The recent photoemission and x-ray absorption results [1] strongly suggest that the antiferromagnetic insulating ground state is not a spin-1/2 antiferromagnetic Mott–Hubbard insulator as assumed in earlier theories [5]. For transition metal compounds, spin and orbital degrees of freedom play an important role in the physical properties [6]. The orbital degeneracy can be lifted by several on-site mechanisms including spin–orbit interaction and Jahn–Teller distortion. In addition to static Jahn–Teller distortion, the dynamic process of virtual distortion also mediates the exchange interaction of pseudospins on adjacent sites.

2. Theory

In V_2O_3, each vanadium atom is surrounded by an octahedron of oxygen atoms. The oxidation state of the vanadium ion is V^{3+} which has the $3d^2$ electronic configuration. The orbitally degenerate d electronic level in the presence of an octahedral crystal field is split into a triply degenerate (t_{2g}) level and a doubly degenerate (e_g) level with t_{2g} lying lowest. The V^{3+} ion, therefore, in an octahedral field has the $(t_{2g})^2$ configuration and, according to Hund's mechanism, the ground term is $^3T_{1g}$. This term has total spin $S = 1$ and total orbital angular momentum $L = 1$ but with a negative sign [7]. So at each site where V^{3+} is situated one can associate a ^3P atomic or ionic term with an effective angular momentum $L = 1$ as the T_{1g} state is isomorphous [7] with the P state. Using this term for a given site and taking into account the spin–orbit interaction, exchange interactions between two V^{3+} ions are considered in the present investigation. As the ground state is an orbital triplet, it can be split into a doublet (^3E_g) and a singlet ($^3A_{2g}$) by an axial distortion. This is also included in the present model. The effect of the lower-symmetry field is treated in the operator equivalent form and interaction between two V^{3+} ions is introduced via the Heisenberg exchange interaction. All of these interactions (lower-symmetry field, spin–orbit and exchange interaction) are treated on the same footing, taking $^3T_{1g}$ to be the unperturbed state. The lower-symmetry field is such that the ground state is a doublet (^3E_g).

In V_2O_3 there is considerable overlap of E_g orbitals in the basal plane, as the bases are of x, y symmetry [7] and as a result the exchange interaction is enhanced. This might be responsible for the higher transition temperature as observed in V_2O_3 ($T_N \sim 150$ K). This type of magnetic transition is treated in a theory [8] which goes beyond mean-field theory by introducing fluctuation to some extent. In this theory, the correlation effect is introduced by a temperature-dependent correlation parameter which is determined self-consistently via the fluctuation-dissipation theorem. In this theory a local moment is developed in the magnetically ordered phase and vanishes at the transition temperature.

The effective Hamiltonian at the ith lattice site occupied by a V^{3+} ion is given by [9]

$$H_i^{eff} = \Delta[(L_i^z)^2 - 2] + \lambda \vec{L}_i \cdot \vec{S}_i - J \sum_j \vec{S}_i \cdot \vec{S}_j \tag{1}$$

assuming exchange interaction to be isotropic. Here Δ is the lower-symmetry crystal-field parameter, λ is the spin–orbit parameter and J is the exchange parameter. Using the correlated effective-field (CEF) approximation [8, 9] the above Hamiltonian reduces to

$$H_i^{CEF} = \Delta[(L_i^z)^2 - 2] + \lambda \vec{L}_i \cdot \vec{S}_i - J \sum_{j,\gamma} \alpha^\gamma (S_i^\gamma)^2 - 2J S_i^\gamma \sum_{j,\gamma} (\langle S_j^\gamma \rangle - \alpha^\gamma \langle S_i^\gamma \rangle) \tag{2}$$

where j is the number of nearest neighbours and γ stands for the Cartesian coordinates. Incorporating the magnetic structure of V_2O_3 in the antiferromagnetic insulating phase, the above Hamiltonian becomes

$$H_i^{eff} = \Delta[(L_i^z)^2 - 2] + \lambda \vec{L}_i \cdot \vec{S}_i - 3J(\alpha^\parallel - \alpha^\perp)(S_i^z)^2 - 6J(1 - \alpha^\parallel)\langle S_i^z \rangle S_i^z \tag{3}$$

where $\alpha^z = \alpha^\parallel$ and $\alpha^x = \alpha^y = \alpha^\perp$ and $\vec{z}$ is the direction in which spin moments are aligned in the ordered phase. The correlation parameters $\alpha^\parallel$ and $\alpha^\perp$ are determined self-consistently by using the fluctuation-dissipation theorem [8, 9].

Using this effective Hamiltonian, the static magnetic susceptibility is given by [10]

$$\chi^\gamma(\vec{q}) = \frac{1}{kT}\left[\langle\langle \mu_i^\gamma : \mu_i^\gamma \rangle\rangle - \frac{[J(\vec{q}) - \alpha^\gamma J(0)]\langle\langle \mu_i^\gamma : S_i^\gamma \rangle\rangle^2}{kT - [J(\vec{q}) - \alpha^\gamma J(0)]\langle\langle S_i^\gamma : S_i^\gamma \rangle\rangle}\right] \tag{4}$$

where $J(\vec{q}) = \sum_{nn} J e^{i\vec{q}\cdot\vec{\delta}}$ and $\vec{\mu}_i = \kappa\vec{L}_i + 2\vec{S}_i$, $\kappa = -1$, in the present calculation. The correlation parameters are determined self-consistently from the equation

$$\alpha^\gamma = \sum_{\vec{q}} \frac{J^\gamma(\vec{q})kT}{kT - 2(J^\gamma(\vec{q}) - \alpha^\gamma J^\gamma(0))\langle\langle S_i^\gamma : S_i^\gamma\rangle\rangle} \Bigg/ \sum_{\vec{q}} J^\gamma(0). \qquad (5)$$

For any operators $\vec{A}$, $\vec{B}$, the following hold good:

$$\langle\langle\vec{A} : \vec{B}\rangle\rangle = \langle\vec{A} : \vec{B}\rangle - \langle\vec{A}\rangle\langle\vec{B}\rangle \qquad (6)$$

$$\langle\vec{A} : \vec{B}\rangle = \sum_n \rho_n \Bigg[A_{nn}B_{nn} + kT\sum_{m\neq n}(A_{mn}B_{nm} + A_{nm}B_{mn})/E_m - E_n\Bigg] \qquad (7)$$

$$\langle\vec{A}\rangle = \sum_n \rho_n A_{nn} \qquad (8)$$

where ρ_n denotes the probability of occupation of the eigenstate $|n\rangle$ of the effective Hamiltonian (3).

3. Results and discussion

Considering the spin–orbit parameter λ to be the free-ion value and Δ to be such that E_g is the ground state, J is fixed in such a way that the antiferromagnetic-to-paramagnetic transition takes place at 150 K as observed in V_2O_3. The uniform susceptibility and correlation parameters calculated for the range of temperature 0–300 K are shown in figure 1 and figure 2 respectively. The local spin moment developed is shown in figure 3 which indicates a jump in the order parameter. In the present calculation a honeycomb lattice is considered where nearest-neighbour V^{3+} ions are arranged in a triangular lattice [1]. The parameters used in this calculation are $\Delta = -550$ K, $\lambda = 110$ K and $J = 56.7$ K which explain the magnetic properties of the insulating phase fairly well [11, 12]. The experimental results [11] for the
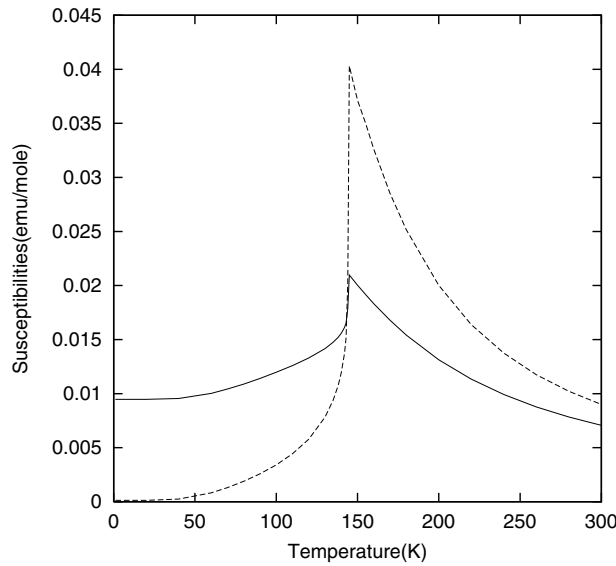

Figure 1. Variations of the susceptibilities with temperature. The full line represents the results for $\chi^\perp$ and the broken one those for $\chi^\parallel$.
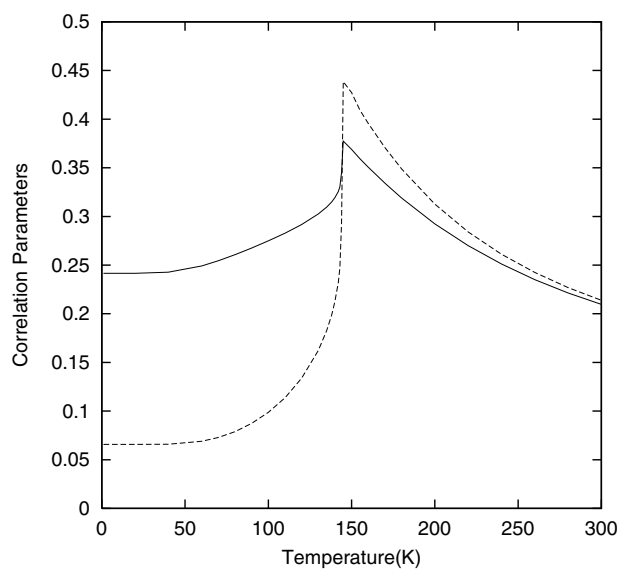
Figure 2. Variations of the correlation parameters with temperature. The full line represents the results for $\alpha^\perp$ and the broken one those for $\alpha^\parallel$.
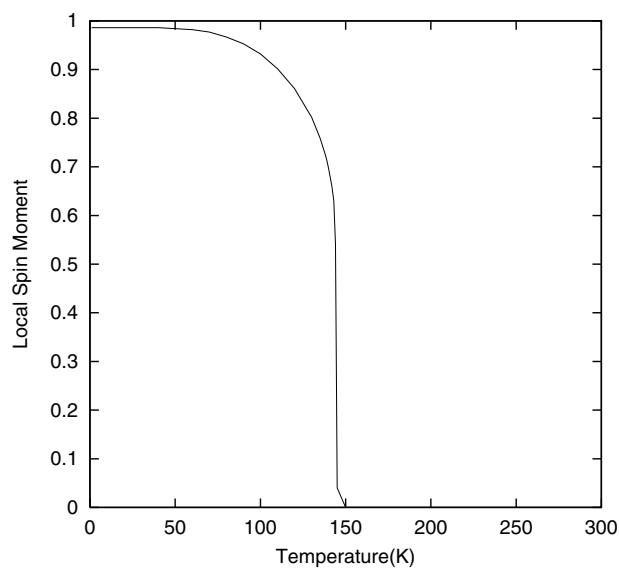

Figure 3. Variation of the local spin moment with temperature.

susceptibility along the direction perpendicular to the basal plane are shown in figure 4 and the local moments observed [12] from the neutron scattering experiment are shown in figure 5. The results indicate that there is qualitative agreement with the theoretical results. The transition temperature is, of course, modified by later experiments. The E_g orbitals are confined to the basal plane and, as a result, the overlaps of the E_g orbitals of two different atoms also lie in this plane. A_{2g} orbitals, on the other hand, are directed [13] perpendicular to the basal plane and their overlap lies in that direction. Since the orbitally degenerate level E_g is responsible for
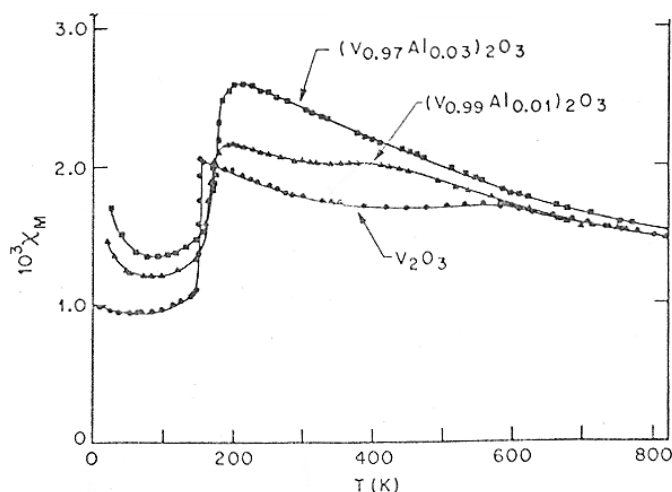
Figure 4. The experimental susceptibility in the direction perpendicular to basal plane.
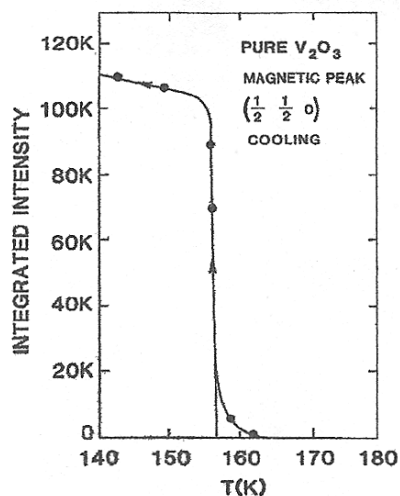

Figure 5. The temperature dependence of the (0.5, 0.5, 0) magnetic intensity.

the metallic character [1], the 2D approximation is accurate enough to explain the magnetic properties of the insulating phase. The present model is, however, incapable of explaining the magnetic properties of the metallic phase. Our model, though it leads to a spin triplet and an orbitally doublet state being associated with each V^{3+} ion, shows a basic difference from earlier models [1, 13]. In our calculation, many-electron coupling at a single site is considered prior to the trigonal distortion, in contrast to the case for recent models proposed to describe the metallic [1] and insulating phases [13] of V_2O_3.

A very recent study [1] on V_2O_3 reveals a new concept of orbital ordering in conformity with the present model. In the present investigation, magnetic properties have been studied in two dimensions and the results suggest that strong correlations of two electrons on a single

site as well as on different sites are important. So in the metallic phase, orbital ordering of the $S = 1$ state and not of the $S = 1/2$ state is to be considered. In V_2O_3 the orbital ordering may be induced by the electron–phonon interaction and/or the electron–electron interaction and it can couple with the magnetic ordering strongly [14]. The origin of the exchange interaction lies in the superexchange interaction between the magnetic ions (V^{3+}) via the ligands (O atoms). This interaction is appreciable in this compound as there is a considerable overlap of magnetic orbitals of x, y symmetry [7] and ligand orbitals having p character in the basal plane which means that the orbital ordering is related to superexchange interaction. The orbital moment plays a vital role [15–17] in V_2O_3 and also in perovskite-type manganites which show the colossal-magnetoresistance effect [18]. It appears that orbital degeneracy of d electrons, which is lifted by a crystal field (static Jahn–Teller distortion) and which causes an orbital overlap between the magnetic ions via the ligands, is responsible for the giant magnetoresistance.

Acknowledgment

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