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Observation of local magnetic moments in the Mott transition of V_2O_3 by means of 3s photoemission

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The 3s and 3p photoelectrons have been measured in pure and Cr-doped V_2O_3, in the antiferromagnetic insulator, paramagnetic metal, and paramagnetic insulator phases. It is found that 3s photoemission provides us with information about local magnetic moments created by 3d electrons in these materials. They are smaller by about 15–25 % in the metal phase than those in the insulator phases. The observed results are discussed in conjunction with the Mott transition and the importance of the spin-fluctuation effect is emphasized.

It is well known that a metal-insulator transition takes place in V_2O_3 at around 150 K from an antiferromagnetic insulator (AFI) to a paramagnetic metal (M). If a V_2O_3 sample is doped with Cr impurities, the phase transition is drastically modified.[1] For example, V_2O_3 doped at a concentration of 1.5 mol % Cr has another paramagnetic insulator (I) phase above the M phase. This second phase transition occurs around 250 K. It is believed that the metal-insulator transitions at both transition temperatures are the typical Mott transitions, which are governed only by the competition between the intra-atomic Coulomb energy (U) of 3d electrons and the width of the 3d band (W).

However, it is puzzling that no change occurs in the valence-band spectrum of V_2O_3 across the metal-insulator transition[2-4] despite a jump[5] in the electric conductivity by as large as seven or eight orders of magnitude. This is accompanied by the intriguing fact that a definite Fermi edge has not been observed in the M phase, nor has a clear band gap been observed across the Fermi level in the I phase. On the contrary, the valence-band spectrum of VO_2 shows a clear Fermi edge in the M phase and a wide band gap in the I phase.[2] Obviously, the definite contrast of the spectra between these two materials lies in the different origins of their phase transitions:[2] The phase transition of VO_2 is mainly due to lattice distortions and that of V_2O_3 is mainly due to the Mott transition. It is expected that the change in the photoelectron spectrum of the valence band, if any, should directly reflect the change in the band structure across the metal-insulator transition. However, the expected change in the electron correlation energy is not manifest in the observed valence-band spectra.

Many years ago, van Vleck[6] showed that the 3s photoelectron spectrum of a 3d transition-metal ion conveys information about the spin states of 3d electrons. He assumed the 3s line to be split into two component lines by the exchange interaction, $G^2(3s,3d)$, between a 3s electron and a 3d electron in the final state with a 3s hole and $3d^n$ electrons. The intensity ratio between the doublet components is equal to $S/(S+1)$, in which S is the total spin of $3d^n$ electrons. The magnitude of the energy splitting is given as

$$\Delta E = [(2S+1)/5]G^2(3s,3d) . \tag{1}$$

Equation (1) suggests that the exchange splitting of the 3s line is a good measure of the magnitude of S. Thus, many experiments[7-10] on various transition-metal compounds have been carried out, with the specific aim of establishing their effects. They are mostly concerned with the relation between the 3s splitting and the magnetic moment (μ) which is crucially connected with the value of S. However, it has been demonstrated that ΔE is not directly related to the local magnetic moment.[10] There is no experimental evidence indicating that the 3s photoelectron spectrum is a simple indicator of the spin state. In particular, the magnitude of the total spin, $\sqrt{\langle S^2 \rangle}$, had not yet been measured experimentally, nor calculated theoretically, above and below the critical temperature of the Mott transition.

Recently, we found a good example that photoelectron spectra are useful for analyzing the metal-insulator transition. In this paper, the 3s and the 3p photoelectron spectra of pure and Cr-doped V_2O_3 are presented. They are measured with a high resolution by using undulator light. Our purpose is to confirm that the change in the 3d spin states across the metal-insulator transition does show up in the 3s photoelectron spectra in these materials. Our data remarkably show that the 3s spectra are clearly distinguishable from the 3p and valence-band spectra.

Single crystals of pure and 1.5 mol % Cr-doped V_2O_3 were grown in a halogen-arc-image furnace. Photoemission experiments were performed at beam line BL-19A of the Photon Factory, where a revolver undulator is used as a light source.[11] Since 3*s* photoemission from vanadium ions is quite weak, intense undulator light is required to measure it with high resolution and precision.

Figure 1 shows the 3*s* photoelectron spectra of V_2O_3 measured at 200 and 77 K with 160 eV excitation and overall resolution of 350 meV. It is recognized in Fig. 1 that the profiles of the two spectra measured at different temperatures are different from each other. In the spectrum in the AFI phase, a doublet structure with features around 69 and 71 eV is discernible. On the other hand, the spectrum in the *M* phase does not show clear doublet structure. Since the spectrum has an asymmetric line shape with a bulge on the high binding energy side of the peak, we ascribe this asymmetric line shape to the unresolved doublet lines. The energy separation between the component lines in the *M* phase seems to be smaller than that in the AFI phase.

In order to resolve the doublet structure, we decomposed the spectra into two component lines with the Doniach-Šunjić (DS) line shape[12] convoluted with a Gaussian broadening function representing the instrumental resolution. Fits of the data were made by least-squares adjustment, where constraints were imposed such that the widths as well as the singularity indices (α) of the two component lines are taken to be equal. The slopes of the background were determined by a straight line drawn between the data points at 62 and 88 eV. The heights of the background were given as adjustable parameters and their values were determined along with other parameters by the least-squares adjustment. The estimated values of ΔE and α are determined within the errors of ± 0.02 and ± 0.01 eV, respectively. In Fig. 1, the background is illustrated by dashed-dotted lines and the two component lines are shown by dots and dashes. The sums of the Gaussian-broadened DS lines shown by solid lines are found to reproduce the experimental spectra well. Through this decomposition and data fitting, parameters describing the exchange doublets of the 3*s* photoemission lines of vanadium ions are obtained. They are shown in Table I.

The exchange splitting energy ΔE is found to be 2.36 eV in the AFI phase. This magnitude is a little smaller than the value[7,13] of ΔE for transition-metal ions having the $3d^2$ configuration, which is evaluated to be about 2.5 eV by extrapolating the values for highly ionic transition-metal ions having the $3d^3$, $3d^4$, $3d^5$, and $3d^6$ configurations. On the other hand, the value of ΔE in the *M* phase is found to be 1.98 eV and smaller by 0.4 eV than that in the AFI phase. According to Eq. (1), the change in ΔE is caused by a change in either *S* or $G^2(3s,3d)$. Since $G^2(3s,3d)$ is determined by electronic eigenfunctions localized on a vanadium ion, it appears natural to assume that $G^2(3s,3d)$ is not affected appreciably by the metal-insulator transition. This conclusion is supported by the observation that the 3*p* photoemission line does not change across the metal-insulator transition, as will be shown later, and consequently $G^{1,3}(3p,3d)$ does not change. In this way, it is concluded that the change in ΔE is mainly due to the change in the total spin *S*.

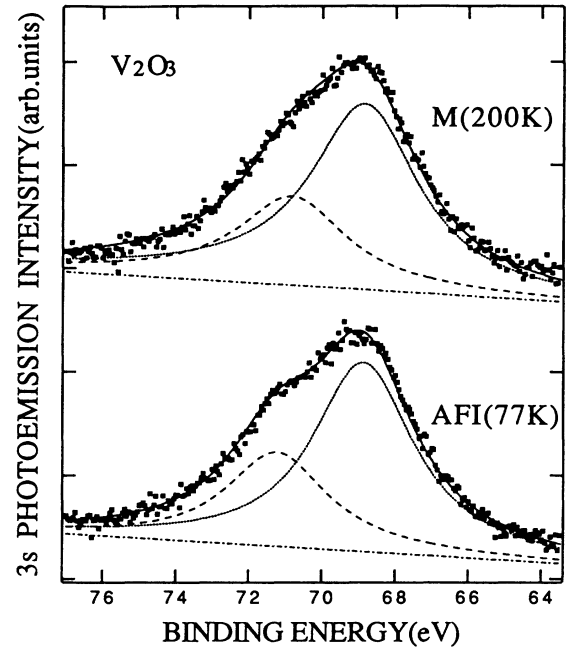

FIG. 1. Energy distribution curves of 3*s* photoelectrons of a pure V_2O_3 crystal measured at 77 K (AFI phase) and 200 K (*M* phase). Dash and dot lines are those decomposed with the Gaussian-broadened Doniach-Šunjić line shapes. Dashed-dotted line represents the background. Solid line illustrates the sum of these lines.

The intensity ratio in the AFI phase is found to be 0.5, which is equal to the value of $S/(S+1)$ for $S=1$ corresponding to that of a V^{3+} ion. In the *M* phase, the intensity ratio is reduced to 0.48.

TABLE I. Estimated parameters describing exchange doublets of the 3*s* photoelectron spectra for pure and Cr-doped V_2O_3. Estimated width of the Lorentzian function involved in the Doniach-Šunjić function is 1.65 ± 0.03 eV. α is the threshold index that represents the asymmetry of the line shape.

	V_2O_3		Cr-doped V_2O_3		
	AFI (77 K)	*M* (200 K)	AFI (77 K)	*M* (200 K)	*I* (297 K)
Splitting energy ΔE (eV)	2.3	1.98	2.30	2.08	2.30
Intensity ratio	0.50	0.48	0.50	0.46	0.49
Threshold index α	0	0.05	0	0.08	≤ 0.01

The singularity index α is estimated to be 0 in the AFI phase. This means that the line shape is symmetric. The line becomes slightly asymmetric in the *M* phase. This fact shows that the asymmetry is brought about in accord with the appearance of the Fermi surface in the *M* phase. Since itinerant electrons participating in the scattering pertinent to the DS process are mostly correlated 3*d* electrons, the expected value of the phase shift contributing to the critical exponent is small. The magnitude of this parameter is much smaller than those of other metallic materials.

In the case of Cr-doped V_2O_3, the 3*s* doublet structure is also observed. This is shown in Fig. 2. The aspect of the change in the doublet structure across the metal-insulator transition is very similar to the case of pure V_2O_3. The ΔE is estimated to be 2.30 eV in the AFI phase and becomes 2.08 eV in the *M* phase. In the *I* phase, it recovers the larger value of 2.30 eV. The change of ΔE across the metal-insulator transition is 0.22 eV, which is slightly smaller than that of pure V_2O_3. This reminds us of the fact that the electric conductivity is smaller in Cr-doped V_2O_3 than in pure V_2O_3. Furthermore, the amounts of the splitting in different samples in the AFI and *I* phases are very close to one another, thus suggesting that the mechanisms of the two phase transitions are similar, regardless of the different magnetic orders. In the case of parameter α in the *I* phase, fitting is possible in a range between 0 and 0.01, while ΔE remain almost unchanged.

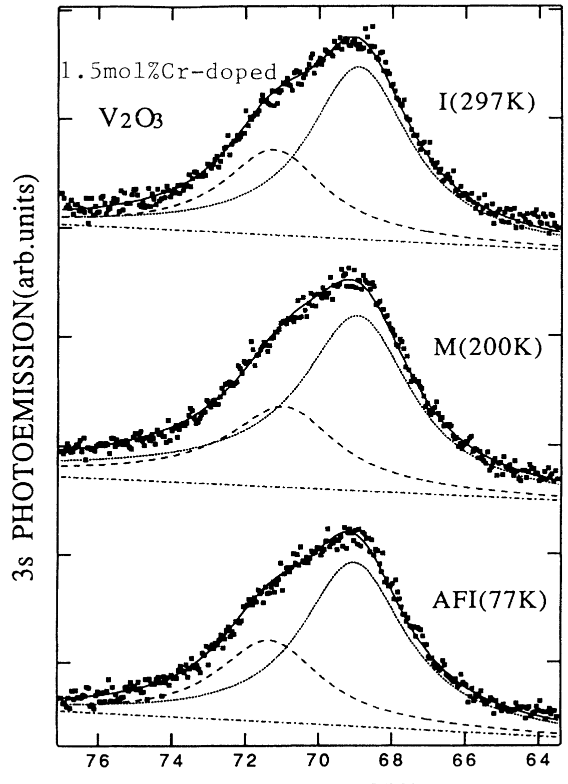

FIG. 2. Energy distribution curves of 3*s* photoelectrons of a V_2O_3 crystal doped with a Cr impurity by 1.5%. Measurements were carried out at 77 K (AFI phase), 200 K (*M* phase), and 297 K (*I* phase). Dash and dot lines are those decomposed with the Gaussian-broadened Doniach-Šunjić line shapes. Dashed-dotted line represents the background. Solid line illustrates the sum of these lines.

The well-known value of the effective Bohr-magneton number for a free V^{3+} ion is $2.83\mu_B$. Since ΔE is about 2.5 eV for the V^{3+} ion which have the total spin of unity, as mentioned before, the value of effective Bohr-magneton number in V_2O_3 can be obtained from the measured value of ΔE. In this way, the effective Bohr-magneton number of pure V_2O_3 is estimated to be $2.7\mu_B$ in the AFI phase and $2.2\mu_B$ in the *M* phase. In the case of Cr-doped V_2O_3, it is $2.6\mu_B$ in the AFI and *I* phases and $2.3\mu_B$ in the *M* phase. On the other hand, the Curie constant[14] of V_2O_3 gives us a value of $2.37\mu_B$ as the effective Bohr-magneton number in the *M* phase. Thus, the local moments estimated from the 3*s* photoemission and the Curie constant coincide satisfactorily with one another. The 3*s* photoemission clearly shows the existence of the local moments even in the *M* phase; the transverse components of fluctuating local moments are the origin of the Curie constant.

The fact that the local moment obtained from the 3*s* photoelectron spectrum is close to the value estimated from the Curie constant conflicts with the result of a neutron-scattering measurement.[15] By analyzing spin-flip processes in neutron scattering, Moon[15] showed that the local magnetic moment in the AFI phase of V_2O_3 is $1.2\mu_B$, which is much smaller than the value obtained by 3*s* photoemission. This discrepancy remains open as a future problem. It should be noticed that the 3*s* photoemission measures the moment in a single vanadium ion in a very short time, while the neutron-scattering measures the ordered moment averaged over a long distance in a crystal. Furthermore, why this value should be much smaller than the value obtained by 3*s* photoemission in the *M* phase is not presently understood.

It is interesting that the valence-band photoelectron spectra of V_2O_3 do not provide us with information on the metal-insulator transition because they exhibit very little change across the metal-insulator transition. This fact is favorable for the viewpoint that the spin fluctuation of 3*d* electrons is important in the mechanism of the metal-insulator transition rather than the change in energy-band structure. It has already been pointed out by NMR experiments[16] that the spin-fluctuation effect is important in the *M* phase of V_2O_3. We interpret the reduction in the value of *S* in the *M* phase in terms of the spin fluctuation to be caused by 3*d* electrons hopping from site to site. To date there is no quantitative theory that predicts the magnitudes of the local moments before and after the metal-insulator transition.[17,18]

The effect of charge fluctuation on the 3*s* photoelectron spectra of metallic materials was studied in detail by Kakehashi, Becker, and Fulde.[18] According to them, the charge fluctuation effect becomes evident as the ratio U/W decreases, and two features occur in addition to the exchange-split lines. They are ascribed to the $n-1$ and $n+1$ states in an ion, where n is the number of 3*d* electrons in ground state of an ion. In the case of V_2O_3, for which U is close to W, the charge fluctuation is suppressed by the electron correlation.

Figure 3 shows the $3p$ photoelectron spectra. The $3p$-multiplet spectra consist of two parts extending over 20 eV. The part at low binding energies has three features A, B, and C. The feature D at high binding energies is weak and broad. They do not seem to change across the metal-insulator transition. The difference spectrum obtained by subtracting the spectrum of the insulator from that of the metal is also shown in Fig. 3 by the solid line above the observed spectra. It hardly has any features at all. This is quite puzzling. The changes of the $3s$ spectra indicate that the total spin changes by about 15% upon the Mott-type transition in V_2O_3. The overlap of complex multiplet lines[19] forming the $3p$ spectra and the lifetime effect may smear out the change of the multiplets. The $3p$ photoemission of Cr-doped V_2O_3 was also measured.[20] The spectrum is found not to change across the metal-insulator transition.

Yamaguchi, Shibuya, and Sugano[19] calculated the $3p$-multiplet structures of transition-metal ions with the $3p^5 3d^n$ configuration for all n. They showed that the spread of the $3p$-multiplet structures depends mainly on the Coulomb energy $F^2(3p,3d)$ and the exchange energies, $G^1(3p,3d)$ and $G^3(3p,3d)$. The calculated spectra of a V^{3+} ion are shown by the vertical bars and the solid line in Fig. 3. The calculated spectrum is consistent with the experimental spectrum, although configuration mixing should be taken into account in order to achieve better agreement between them. The fact that the $3p$ spectrum does not change suggests that $F^2(3p,3d)$ and $G^{1,3}(3p,3d)$ are unaffected by the metal-insulator transition at all, as mentioned before.

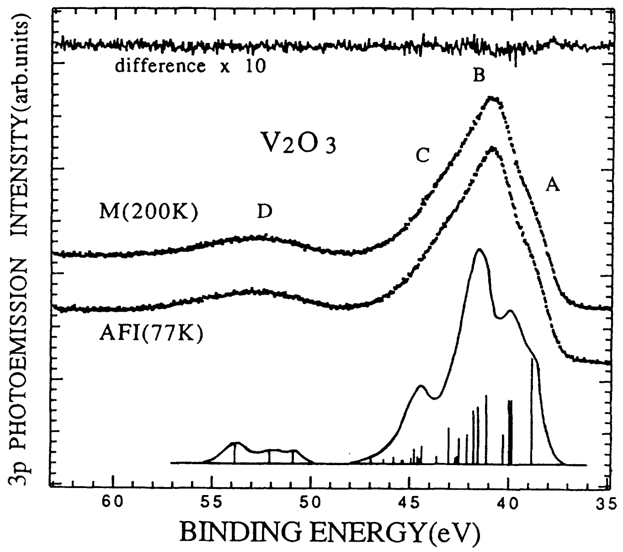

FIG. 3. Energy distribution curves of $3p$ photoelectrons of a pure V_2O_3 crystal measured at 77 K (AFI phase) and 200 K (*M* phase). The solid curve exhibited above the observed spectra illustrates the difference spectrum between two spectra in ten-times expanded scale. Vertical bars and a solid line above it illustrate the calculated line distribution and its convoluted curve.

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