Electron Correlation Effects in Resonant Inelastic X-Ray Scattering of NaV_2O_5

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Element- and site-specific resonant inelastic x-ray scattering spectroscopy (RIXS) is employed to investigate electron correlation effects in NaV_2O_5. In contrast to single photon techniques, RIXS at the vanadium L_3 edge is able to probe d-d^* transitions between V d-bands. A sharp energy loss feature is observed at -1.56 eV, which is well reproduced by a model calculation including correlation effects. The calculation identifies the loss feature as excitation between the lower and upper Hubbard bands and permits an accurate determination of the Hubbard interaction term $U = 3.0 \pm 0.2$ eV.

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Orthorhombic NaV_2O_5, with symmetry P_{mmn}, is a new type of Mott insulator and possesses many exotic properties [1,2]. It exhibits a spin-Peierels-like phase transition [3], but does not have some typical features shown by $CuGeO_3$ [4] such as change of the transition temperature with magnetic fields [5]. As in many Mott insulators, the strong correlation in NaV_2O_5 splits its original d_{xy} band into two new Hubbard subbands d_{xy} and d_{xy}^*, and opens a gap around the Fermi surface. Such a gap is strong evidence of the electron correlation effect. It probably cannot be probed optically; due to the dipole selection rule, a direct transition between d_{xy} and d_{xy}^* is very weak if not completely forbidden. In particular, recent work pointed out that the 1.0 eV peak in the optical absorption spectrum does not originate from the so-called d-d transition as previously suggested [6], but is related to the number of V^{5+} ions [2]. The correlated nature of NaV_2O_5 was also investigated by angular-resolved-photoemission spectroscopy (ARPES) [7], but the results may be compromised by charging effects. Even assuming no charging effect, ARPES probes only the occupied states with little information on the unoccupied bands [8]. Electron energy-loss spectroscopy (EELS) faces a similar difficulty as ARPES imaging only the unoccupied states. Furthermore, the elastic contribution and surface losses make EELS unable to measure at zero momentum transfer [8,9]. To this end, a direct probe of the correlation effect is yet to come.

Element- and site-specific resonant inelastic x-ray scattering spectroscopy (RIXS) [10] is a powerful tool to *directly* probe those optically *inaccessible* bands in complex materials. It can project out the density of states element by element, which can be directly compared to the theoretical calculation. In this Letter, we use RIXS to directly probe electronic excitations across the Fermi level in NaV_2O_5. The RIXS spectra taken at the vanadium L_3 edge show two principal features. A broad band located between -4 and -10 eV on the energy loss scale derives from strongly hybridized V-d/O-p bands. A smaller energy loss feature at -1.56 eV, which resonates strongly in a narrow range of incident photon energies near threshold, is the focus of this paper. It is associated with a narrow band derived predominantly from V-d_{xy} orbitals with little contribution from O-p orbitals. In the absence of correlation effects, the band spans the Fermi level. Correlation effects split the band into upper and lower Hubbard bands. Because of the lack of O-p hybridization with the vanadium orbitals creating this band, we are able to use a simplified model that suppresses the V-O interactions but accurately describes the d_{xy} band at the Fermi level and accounts for correlation effects between vanadium atoms. The model calculation accurately reproduces the -1.56 eV energy loss feature with a Hubbard interaction term of $U = 3.0 \pm 0.2$ eV, and identifies this energy loss with a d-d^* excitation between the lower and upper Hubbard bands.

Resonant inelastic x-ray scattering is a photon-in and photon-out technique [10]. An incoming photon first excites electrons from a core level of one element of the compound to the unoccupied bands. Thus, this is an element-specific technique. In the RIXS process, an electron from occupied bands recombines with the core hole, leaving an electron in the unoccupied bands and a hole in the occupied bands. The energy loss between the incident photon and emitted photon energies measures the difference between the occupied and unoccupied bands. The smallest energy-loss peak corresponds to the lowest excitation between states with the angular momentum change of $\Delta l = 0, \pm 2$. If the excited electron directly recombines with the core hole without involving the valence electrons, this gives an elastic peak whose energy is exactly equal to the incident photon energy.

Single crystals of NaV_2O_5 were prepared at the Oak Ridge National Lab. The samples were characterized by x-ray diffraction, specific heat and magnetic susceptibility measurements, and were cleaved along the c direction to provide clean and flat [001] surfaces containing the a and b axes. The long dimension was along the b axis and the shorter dimension along the *a* axis. Our measurements were performed at the soft x-ray spectroscopy end station on Undulator Beam Line 8.0 at the Advanced Light Source (ALS) located at the Lawrence Berkeley National Lab. Our monochromator was calibrated with Ti-*L* edge of TiO_2 and compared with the V-*L* edge of V_2O_5; the spectrometer was calibrated according to the elastic peak. Monochromatized light from the undulator is incident on samples placed within a few mm of the entrance slit of an emission spectrometer. The incident beam is *p* polarized and the emission spectrum is taken at 90° from the incident beam.

Figure 1(a) shows the V-L_3 emission spectra versus emitted photon energies. The incident photon energies are labeled from *a* to *g*. The vertical bars mark the position of the elastic peak located at the incident photon energy. The excitation energies are also indicated on a plot of the total fluorescent yield in Fig. 1(b). The emission spectra display two main features: peak *A* on the left-hand side and peak *B* on the right-hand side. At energies below about 516 eV, both peaks track the incident photon energy to higher energies in the way characteristic of RIXS spectra, where there is a fixed energy separation between incident and emitted photons [11]. Above about 516 eV, the spectra evolve into soft x-ray normal fluorescence (SXF) spectra in which incident and emitted photons are decoupled and the spectral features are fixed in energy. In the transition region, both RIXS and SXF features may be present in the spectra as is observed for peak *B* for incident energies of 518 and 519 eV. Peak *A* results from the hybridized oxygen 2*p* and vanadium 3*d* bands (see the lower left part of Fig. 2). Elsewhere [12], we explore in more detail the density of states information from absorption and SXF spectra taken at both the V-L_3 and the O-*K* edges. Here we concentrate on the particular features associated with peak *B* in the vicinity of the threshold at 516 eV, which provide specific information on correlation effects of the vanadium atoms in this material.

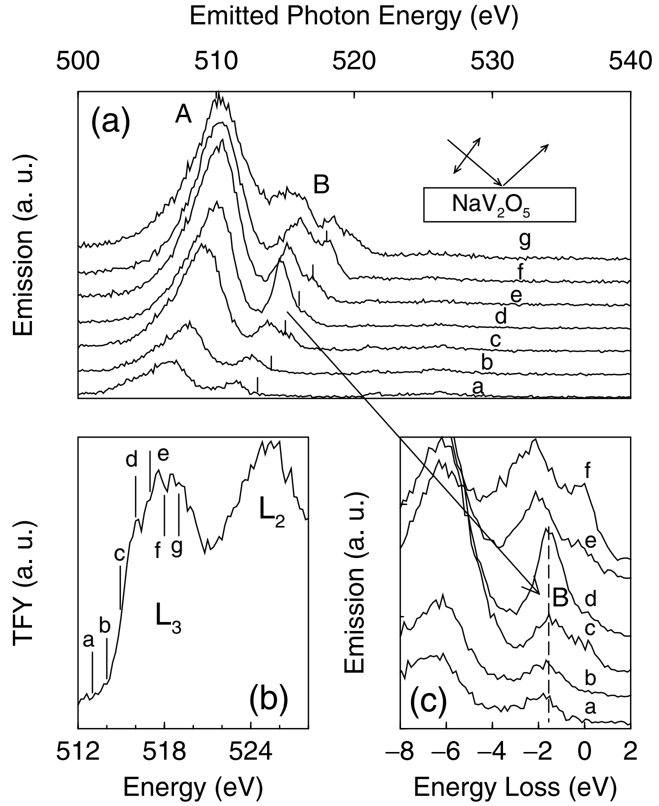

FIG. 1. (a) V-L_3 edge resonant inelastic x-ray scattering spectrum in NaV_2O_5. Incident energies are labeled from *a* to *g*. The vertical bars denote the elastic peak positions. (b) Total fluorescence yield (TFY). (c) Enlarged view of peak *B* on the energy loss scale.

In Fig. 1(c), an enlarged view of peak *B* is shown on an energy loss scale which is calculated by subtracting the elastic peak energies from the inelastic energies on the same emission spectra. In the RIXS region below 516 eV (curves *a*–*d*), a fixed energy loss of $-(1.56 \pm 0.05)$ eV is observed. The peak resonates strongly at 516 eV (curve *d*). As may be seen from Eq. (2) below, the resonance occurs when the energy of incident photons is just sufficient to excite a 2*p* core electron into a real intermediate state. In the present case we believe that this resonance excitation occurs to V-d_{xy} states derived from the upper Hubbard band, with emission occurring from correlated lower Hubbard band states. It is important to note that, although the position and strength of the resonance is effected by core-hole localization in the intermediate state, the observed energy losses involve only the initial and final states of the scattering process. Thus, the measured energy losses do not include the effects of core hole localization and lifetime, and are an accurate measure of the d-d^* excitation between the lower and upper Hubbard bands. In Fig. 2, we illustrate our picture for

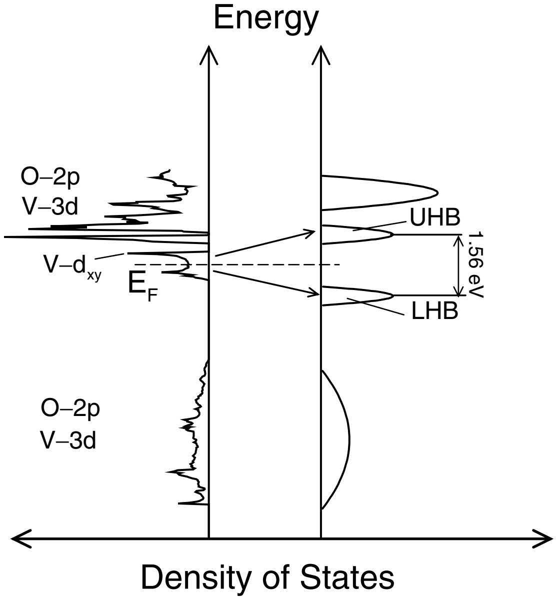

FIG. 2. Correlated picture of NaV_2O_5. Left panel: LDA calculation; right panel: modification due to electron correlation.

interpreting the spectra. Projected to the left is the total density of states calculated using the WIEN97 band structure codes [13]. The lower valence band is formed primarily from V-3d states hybridized with O-2p states. The band spanning the Fermi level is formed from nearly pure V-d_{xy} orbitals that interact along the rungs of the ladderlike structure of NaV_2O_5. The bands above the Fermi level are also formed from strongly hybridized V-d/O-p orbitals. Projected to the right in the figure is our picture of the spectra when correlation is added. The V-d_{xy} band spanning the Fermi level is now split by correlation effects, with the lowest observed energy loss corresponding to the splitting of this band.

Such correlation effects can be better understood within a simple model cluster. In order to do so, we choose a ladder consisting of eight V atoms with a periodic boundary condition along b axis as shown in Fig. 3. Only V-d_{xy} orbitals around the Fermi surface are explicitly taken into account. Oxygen orbitals are suppressed though their presence is partially taken into account by fitting the results to a band calculation. This is a good approximation for the present problem since the V-d_{xy} band dominates around the Fermi surface (see Fig. 2) and there is little contribution from the oxygen bands [12]. Therefore, we focus on peak B in the experimental curve (see Fig. 1).

Within these approximations, we write the Hamiltonian as [9,14–16]

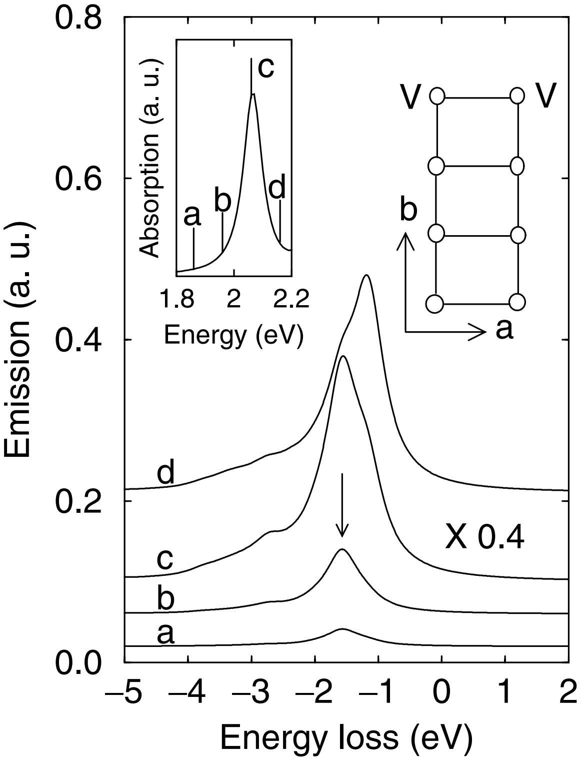

FIG. 3. Correlated model calculation of RIXS. Intensities are in the same but arbitrary units. The arrow denotes the resonant inelastic peak position. Insets: (left) absorption spectrum; (right) used model cluster.

$$H = -\sum_{\langle ij\rangle\sigma} t_{ij}^{a(b)} (c_{i\sigma}^{\dagger} c_{j\sigma} + \mathrm{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\mu \in a,b} V^{\mu} \sum_i n_i^{\mu} n_{i+1}^{\mu}, \tag{1}$$

where the nearest neighbor hopping integral $t_{\langle ij\rangle}^{a(b)}$ along the $a(b)$ direction is obtained by fitting the *ab initio* band structure [1]; the on-site interaction U is from our experiment; the intersite electron correlation along the $a(b)$ direction, $V^{a(b)}$, is obtained from a previous optical study [9,15,16]. To be more specific, we choose $t^a = 0.38$, $t^b = 0.17$, $U = 3$, $V^a = 0.72$, and $V^b = 0.72$ eV. The number of electrons of the system is $N = 4$. All of the operators are standard [15]. Within such a small cluster, we can directly diagonalize the many-body Hamiltonian with the Lanczos recursion method [17] and obtain eigenstates and eigenvalues. The RIXS spectrum is calculated from the Kramers-Heisenberg formula [10,11]

$$S(\omega, \omega') = \sum_f \left| \sum_m \frac{\langle f|p \cdot A|m\rangle\langle m|p \cdot A|gs\rangle}{\omega + E_{gs} - E_m - i\Gamma} \right|^2 \times \delta(E_{gs} + \omega - E_f - \omega'), \tag{2}$$

where $|gs\rangle$, $|m\rangle$, and $|f\rangle$ are initial, intermediate, and final states, and E_{gs}, E_m, and E_f are their energies, respectively; ω and ω' are the incident and emitted photon energies; Γ is the spectral broadening due to the core lifetime in the intermediate state. $p \cdot A$ is the transition operator, which is approximated by a dipole operator. Our approach is similar to a previous calculation [18]. In the intermediate states, the system contains $N + 1$ electrons and one hole in the core level; in the final states, the system has N electrons and the core hole is refilled leaving an electron-hole excitation behind.

In metals, since there is a finite density of states at the Fermi level, RIXS starts from a zero-energy loss. In NaV_2O_5 the local density approximation (LDA) calculation catches almost all the experimental features but predicts a metallic phase around the Fermi level. Consequently, the LDA-RIXS spectrum begins from a zero-energy loss, in contrast to our experimental observation. However, we can recover this missing feature by including electron correlations. The results are shown in Fig. 3, where the intensities are on the same but arbitrary scale, thus they are comparable. The incident energy is labeled from a to d with a strong resonance in curve c. In the inset, incident energies are also marked, where the core level energy is already subtracted from the energy scale. Upon increase in the incident photon energy, the spectrum exhibits a familiar inelastic resonance feature as we have seen in our experiments: The peak tracks the incident photon energy up to the threshold. The prominent feature is a resonant peak which appears at an energy loss of -1.55 eV (see the arrow), which can be directly compared with our experimental value of -1.56 eV. Varying U in the calculation produces a linear change in this energy loss feature. We find that a variation in U of 3.0 ± 0.2 eV corresponds to the experimental uncertainty of the energy loss of $-(1.56 \pm 0.05)$ eV. Previous theoretical and experimental studies have estimated U ranging from 2 to 7 eV [1,2,9,15,16,19]. We believe that our value is soundly based on an appropriate model accurately describing the process being precisely measured experimentally, and thus strongly constrains U to values near 3.0 eV.

Two other weak resonances are apparent in the theoretical emission spectra at about -2.8 and -1.2 eV, respectively. The former one may indicate the continuum edge, but in order to determine this edge accurately, a much larger system which accurately includes V-O interaction is needed. The latter one mainly results from the finite size effect of the cluster used in the calculation. We believe that it becomes relatively weaker as the cluster size is increased and becomes negligible for large clusters. As aforementioned, since the lowest energy loss of the resonant inelastic peak measures the lowest excitation energy, the nonzero energy loss unambiguously establishes a gap is opened. However, if we switch off the electron correlation terms, from Eq. (1) we know that this comes back to the LDA results where the gap is closed and, consequently, the resonant peak starts from the zero-energy loss. This shows the importance of the electron correlation effect. Since around the Fermi level, the density of states is predominantly of d_{xy} characters, the gap must be between the lower Hubbard d_{xy} band and the upper Hubbard d_{xy}^* band. Therefore, our experiment and theory jointly point out an old wisdom [1,20] in NaV_2O_5: the electron correlation splits the original V-d_{xy} bands and drives the system into an insulating phase.

In addition, a decade of experimental work [11] has shown that the RIXS spectra have intensities of the similar magnitude as ordinary SXF spectra since theoretically the matrix elements governing RIXS and SXF are substantially the same except for modifications of spectral shape due to interference effects and enhancements in RIXS spectra due to the resonant denominator. Using the ratio of the RIXS intensity to the SXF intensity, we can estimate the scattering cross section of RIXS. We found that depending on incident photon frequencies, the ratio is about 2–3 times in our experiment, which is compatible with our theoretical estimation of 2–4 times.

In conclusion, our element- and site-specific resonant inelastic x-ray scattering spectrum provides much insight into the complicated electron structure in NaV_2O_5. Electron correlation manifests itself by opening the gap around the Fermi surface. Our study demonstrates the value of soft x-ray spectroscopies for directly probing the correlation effects in these interesting transition-metal oxides [21], high T_c superconductors [8], and GMR materials.

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[1] H. Smolinski *et al.,* Phys. Rev. Lett. **80**, 5164 (1998).

[2] C. Presura *et al.,* Phys. Rev. B **62**, 16 522 (2000).

[3] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).

[4] S. G. Bompadre *et al.,* Phys. Rev. B **61**, R13 321 (2000).

[5] A. N. Vasil'ev *et al.,* Phys. Rev. Lett. **81**, 1949 (1998).

[6] S. A. Golubchik *et al.,* J. Phys. Soc. Jpn. **66**, 4042 (1997); H. Wu and Q. Q. Zheng, Phys. Rev. B **59**, 15 027 (1999); V. C. Long *et al.,* Phys. Rev. B **60**, 15 721 (1999).

[7] K. Kobayashi *et al.,* Phys. Rev. Lett. **82**, 803 (1999).

[8] M. Z. Hasan *et al.,* Science **288**, 1811 (2000).

[9] S. Atzkern *et al.,* Phys. Rev. B **63**, 165113 (2001).

[10] T. A. Callcott and E. T. Arakawa, Phys. Rev. B **18**, 6622 (1978); J. J. Jia *et al.,* Phys. Rev. Lett. **76**, 4054 (1996); J. A. Carlisle *et al.,* Phys. Rev. Lett. **74**, 1234 (1995); A. Kotani and S. Shin, Rev. Mod. Phys. **73**, 203 (2001).

[11] T. A. Callcott, in *Vacuum Ultraviolet Spectroscopy II,* edited by J. A. Samson and D. L. Ederer, Experimental Methods in the Physical Sciences Vol. 32 (Academic Press, New York, 1998), p. 279.

[12] G. T. Woods, G. P. Zhang, L. Lin, and T. A. Callcott, Phys. Rev. B (to be published). A previous LDA + U calculation [A. N. Yaresko *et al.,* Phys. Rev. B **62**, 15 538 (2000)] indicates that the correlation effects push the V-3d/O-2p band above the UHB.

[13] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology, 1997; P. Blaha *et al.,* Comput. Phys. Commun. **59**, 399 (1990).

[14] The core level term is subtracted from the Hamiltonian. The strength of the interaction between the 3d electron and the core hole is unknown at present. Instead of introducing an unknown quantity into our calculation, we leave this for a future study.

[15] M. Cuoco *et al.,* Phys. Rev. B **60**, R8438 (1999).

[16] D. Sa and C. Gros, Eur. Phys. J. B **18**, 421 (2000).

[17] G. P. Zhang, Comput. Phys. Commun. **109**, 27 (1998); G. P. Zhang *et al.,* J. Chem. Phys. **109**, 2562 (1998); G. P. Zhang and W. Hübner, Phys. Rev. Lett. **85**, 3025 (2000); G. P. Zhang, Phys. Rev. B **61**, 4377 (2000).

[18] S. Tanaka *et al.,* J. Phys. Soc. Jpn. **59**, 1488 (1990).

[19] A. Hübsch *et al.,* cond-mat/0105165; P. Horsch *et al.,* Eur. Phys. J. B **5**, 367 (1998); S. Nishimoto *et al.,* J. Phys. Soc. Jpn. **67**, 3679 (1998); V. Yushankhai *et al.,* cond-mat/0008322; Z. S. Popovic *et al.,* Phys. Rev. B **59**, 5333 (1999); N. Suaud *et al.,* Phys. Rev. B **62**, 402 (2000).

[20] J. Hubbard, Proc. R. Soc. London A **276**, 238 (1963); **281**, 401 (1964).

[21] S.-H. Lee *et al.,* Phys. Rev. Lett. **86**, 5554 (2001); R. Valenti *et al., ibid.* **86**, 5381 (2001).