Resonant x-ray-diffraction study of the charge ordering in NaV_2O_5

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We show that in the mixed-valence $3d$ transition-metal oxide NaV_2O_5 undergoing a structural transition, the low-temperature phase results from an effective ordering of the charge. This arrangement and the quantitative evaluation of the atomic charges are determined by using resonant x-ray scattering experiments further analyzed with the help of realistic calculations of the corresponding scattering factors. We have found that this reorganization concerns only a small fraction of electron and is necessary to reconcile all the experimental data.

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I. INTRODUCTION

There is an issue in understanding the charge state in the high- and low-temperature phase of mixed-valence transition-metal compounds. Few experimental techniques can access the actual charge state of a given atom, and most of the accumulated knowledge results from theoretical models[1] and from indirect results based on transport property measurements[2] or from heuristic bond-valence calculations on the crystal structure.[3] Nevertheless, the answer to very simple questions would turn out to be of large relevance in the context of metal-insulator or insulator-insulator phase transitions issued from a charge ordering (CO). For instance, given an average valence state as deduced from charge neutrality considerations of the chemical composition, would the ground state be an effective CO ? If so how are the corresponding electrons arranged ? Are they located in the very localized $3d$ orbital of the transition metal, or in the extended $4s$ or even on the oxygen ligands ? In this paper we claim that resonant x-ray diffraction is able to answer quantitatively these questions in the mixed-valence transition-metal compound NaV_2O_5.[4] In our study, we have found a small but effective ordering occurring mainly in the $3d$ transition-metal orbitals. Such kind of quantitative evaluation is promising for many other compounds exhibiting CO, which range in diversity and physical properties from colossal magnetoresistance manganites, to the astonishingly complex Verwey[5] transition in magnetite.

II. RESONANT X-RAY SCATTERING AND CHARGE ORDERING

X-ray absorption spectroscopies (XAS) and resonant x-ray scattering are extensively used techniques to explore and elucidate the electronic properties of materials.[6,7] In these spectroscopies the incoming photons are absorbed by promoting a core electron to an empty intermediate excited state *f*. When the electron subsequently decays to the same core hole, it emits a second photon with the same energy than the incoming one. This process is virtual and preserves the coherence of the electromagnetic wave. Set in diffraction conditions the associated experimental technique is known as diffraction anomalous fine-structure spectroscopy or resonant diffraction. When the absorption process is considered alone, and therefore losing the coherence properties of the x-ray field, the experimental technique is called XAS or x-ray absorption near edge spectroscopy (XANES) when considering the structure close to the edge. In this low-energy range a higher sensitivity to the electronic configuration around the photoabsorber is expected because the photoelectron probes allowed electronic states very close to the Fermi level as required by the selection rules resulting from the Fermi golden rule. Indeed, by playing with the polarization of the incoming (and eventually outgoing) photon beam, with the different channels of transition (dipole, quadrupole) and with the orientation of the crystal with respect to the photon polarization direction, the probability of transition becomes highly angle dependent. This phenomenon is illustrated by a tensor form of the scattering structure factors, and the analysis of each term of the tensors gives access to specific projections of the electronic states. Although we have performed complete calculations, we will restrict to the dipole approximation for simplicity. The atomic scattering factor (ASF) reads

$$f' + if'' = \sum_{\alpha\beta} \epsilon_\alpha^{o*} \epsilon_\beta^i D_{\alpha\beta}, \tag{1}$$

where α and β are the indices of the coordinates in the orthogonal basis. ϵ^i and ϵ^o stand for the incoming and outgoing polarizations and $D_{\alpha\beta}$ is given by

$$D_{\alpha\beta} = -m_e\omega^2 \sum_{fg} \frac{\langle \psi_g | r_\alpha | \psi_f \rangle \langle \psi_f | r_\beta | \psi_g \rangle}{E_f - E_g - \hbar\omega + i\dfrac{\Gamma(E_f)}{2}}, \tag{2}$$

where E_f, E_g, and $\hbar\omega$ are, respectively, the energies of the intermediate state, the core state, and the photon; m_e is the electron mass and $\Gamma(E_f)$ includes the contribution of the inverse lifetime of all the states involved in the resonant process. The summation over *f* is limited to the unoccupied states. In diffraction, the intensity of the reflections is proportional to the modulus squared of a weighted sum of the ASF:

$$I(\vec{Q};\hbar\omega) \propto \left| \sum_a e^{i\vec{Q}\cdot\vec{R}_a} [f_{0a}(\vec{Q}) + f'_a(\omega) + if''_a(\omega)] \right|^2, \tag{3}$$

where $\vec{R_a}$ stands for the atom a position and $\vec{Q}$ is the diffraction vector. The atomic scattering amplitude is the sum of the Thomson factor f_{0a} and the ASF.

Of particular importance are the *forbidden* Bragg peaks that are extinct off-resonance conditions because of the presence of glide planes or screw axis. For these reflections, the diffracted intensity is related to the difference between ASF of the resonant (or anomalous) atoms. Therefore, these reflections are supposed to be much more sensitive to slight modifications of the crystallographic as well as the local electronic structure. In the absence of new superlattice peaks originating from a phase transition (typically ferrodistortive phase transitions), these *forbidden* Bragg peaks might yield relevant information on the corresponding CO.

This phenomenology has been extensively used in the study of the interplay between orbital, spin, and charge degrees of freedom in transition-metal oxides.[8,9] In particular, it is specially suited to study charge[10] and orbital orderings.[11–13] Nevertheless, apparently contradictory results have led to opposite conclusions on the presence or not of a real CO. Recent resonant diffraction experiments at *forbidden* reflections in Fe_3O_4 have yielded no change in the resonant signal below and above the ordering temperature and it has been concluded that no CO occurs at the Verwey transition.[14] Conversely, resonant-scattering experiments in NaV_2O_5 (Ref. 15) and $La_{1/2}Sr_{1/2}MnO_3$ (Ref. 16) have shown that the energy line shape of some reflections retains close similarities with the derivative of the resonant x-ray scattering factor, a fact which has been interpreted as a signature for the presence of two different V (or Mn) charge states ordered in the lattice. In this paper we shall show that such experimental evidences, a derivative line shape for some reflections, and an absence of modification of the spectra in other forbidden reflections are in fact not contradictory and can be interpreted within the same framework. In order to accomplish this task, we shall proceed in a quantitative analysis of the resonant diffraction experiments with the help of realistic simulations. It will then be possible to evaluate the influence of the different parameters and estimate the effective charge redistribution resulting from the CO transition. The present study concerns NaV_2O_5 but the same kind of analysis must be applied in future to the compounds exhibiting the same trends.

III. APPLICATION

A. Experiment and method of calculation

To illustrate our analysis we shall discuss very recent resonant x-ray-diffraction results in NaV_2O_5 and all the experimental details can be found in Ref. 15. Among the numerous diffraction peaks measured as a function of the incident photon energy and under different photon polarization conditions, we select three of them to illustrate our results. The first one is the $(1,0,0)_c$ *forbidden* reflection which does not exhibit any change through the transition. The incoming photon polarization is along c and the outgoing one is in the scattering plane (σ-π polarization condition). The two other reflections under consideration are superlattice peaks $(15/2,1/2,1/4)_{b,c}$, for which the incoming and outgoing photon polarizations were kept parallel (σ-σ condition). According to the index, the polarization directions are along either the b or c axis. The superstructure peaks appear due to the phase transition, and the energy dependence of the scattered intensity exhibits peculiar features that we examine in detail below. Realistic monoelectronic calculations are performed using the FDMNES code.[17,18] Starting from the atomic positions and an associated electronic density, this code solves the Schrödinger or Dyson equations to determine the intermediate states probed by the photoelectron. The resulting structure factors are evaluated by taking into account the different excitation-deexcitation channels (dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole). Diffracted intensities are calculated with the crystallographic structures corresponding to the high-($Pmmn$, Ref. 19) and low-($A112$ Ref. 20) temperature phases with and without CO. Because the purpose of the present paper is to fit the electronic structure, it is important to define easy-to-handle parameters. We choose the valence orbital occupancy rates (VOOR). The radial shape of the atomic orbitals remains fixed. For any VOOR set, the total electronic density is obtained by simple superposition of the electronic orbital densities weighted by the VOOR. First-guess VOOR values corresponding to the high-temperature (HT) phase are obtained by a fit on the electron density calculated by a LAPW (Ref. 21) band-structure procedure. These orbital occupancies, which reflect the location of the charge in space, are further refined in order to accurately reproduce the experimental curves in the low-temperature phase. The vanadium and oxygen VOOR are then the only adjustable parameters of our calculations. The HT starting values are 2.3 and 1.7 electrons for the $3d$ and $4s$ V atoms, respectively, and 4.6 electrons for the $2p$ O atoms. If one uses the ionic radii as a definition of the atomic spheres, the $4s$ charge (average radius is 1.5 Å, to be compared with the $3d$ average radius, 0.6 Å) lies inside the oxygen atoms. Thus, the V formal charge is $2.7+$ in this context. The sodium atom has no electron in its $3s$ valence orbital and remains $1+$ throughout the study. With this VOOR set, a good agreement is obtained at HT between the calculated (100) reflection, the polarized XANES line shape, and the corresponding experimental spectra. To get such agreement, the finite-difference procedure is used to solve the Schrödinger equation. This technique permits to avoid the muffin-tin approximation on the potential shape. This point is absolutely necessary in such distorted systems.

B. Results and discussion

We now discuss the low-temperature (LT) phase and the starting point is the crystallographic structure as determined in Ref. 19. The most important result is that an explicit CO is absolutely necessary to get a satisfactory agreement with the experiment (Fig. 1). The fit of the experimental data yields two equivalent solutions: (a) The charge exchange is located at the $4s$ vanadium and amounts $\delta = \pm 0.2$ electron and (b) it is located at the $3d$ vanadium and amounts only $\delta = \pm 0.04$ electron. Thus, the CO takes place either in the intermediate region between the oxygen and the vanadium where an

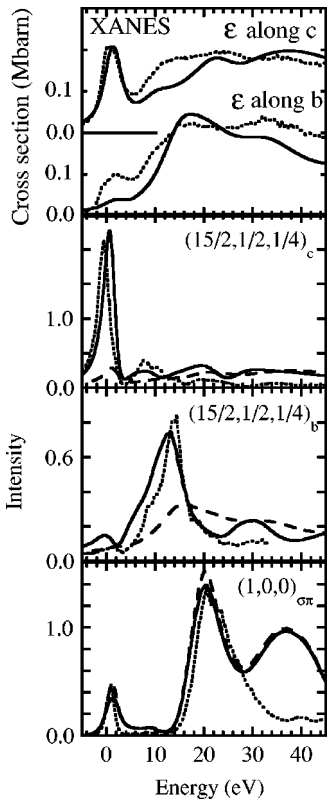

FIG. 1. Experimental and calculated resonant diffracted peak spectra in NaV_2O_5. From bottom to top the (1,0,0) σ-π, $(15/2,1/2,1/4)_c$, and $(15/2,1/2,1/4)_b$ peaks (both measured in the σ-σ configuration) and the XANES cross section are shown. For each reflection the spectra corresponding to the experiment (dotted line) and the calculation in the low-temperature phase with charge ordering (continuous line) and without charge ordering (dash line) are displayed. For the $(1,0,0)_{\sigma\pi}$ reflection the high-temperature structure calculations are not shown as they are practically identical to the LT calculation without charge ordering. The charge-order model yields very few modifications of the signal through the transition for the first peak. The derivative effect for the two last ones cannot be accounted for by a lattice distortion alone, and is best reproduced when different charges are introduced at convenient V sites. The XANES spectra for the polarization ϵ along the *c* and *b* axes are also given. The different calculations at HT and LT with or without charge ordering yields practically the same results.

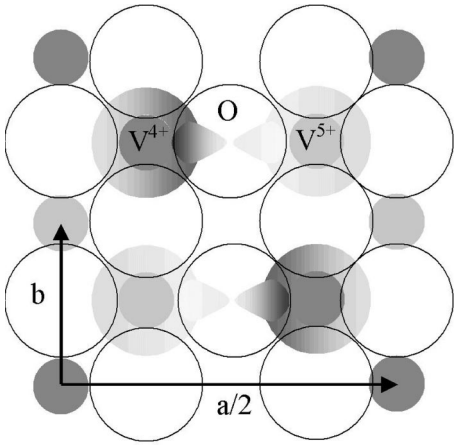

FIG. 2. A sketch of the NaV_2O_5 structure focused around the V^{4+}-O-V^{5+} rungs. All oxygen atoms lie in the same plane, whereas vanadium rungs lie alternatively below and above the oxygen plane. The vanadium (full circles) atoms are surrounded by five oxygen atoms, four shown in white circles on the figure and a fifth one in the apical direction (not shown). The rings show the region where the electronic density is affected by the CO, the difference in density around the vanadium atoms being illustrated by the different gray tones.

atomic assignment of the electron is merely formal (see Fig. 2) or closer to the V atom, in the near empty shells but with a smaller magnitude. In any case, the bridging oxygen located in the rung of the ladder, being the atom that experiences the largest displacement at the phase transition (0.05 Å towards the V^{5+}, that is, five to ten times more than the other atoms), is suspected to participate in the electronic rearrangement as well. Thus, the electronic reorganization we propose does not concern isolated atoms but the entire rung of the ladder, with the center of gravity of the electronic density displaced in the opposite direction than that of the bridging oxygen, i.e., toward the V^{4+} atom. Taking into account the experimental resolution, the choice among the two proposed solutions cannot be safely done. Nevertheless, the second one with a CO on the $3d$ orbital is in agreement with that obtained by Suaud and Lepetit[22] on the basis of *ab initio* calculations using large configuration-interaction methods on embedded fragments. These authors found a $\pm 0.04e$ CO in the $3d$, in excellent agreement with the present study. They have also shown that the modification of the magnetic properties at the phase transition is due to the redistribution between the different *d* orbitals, keeping the total *d* charge only slightly modified. We want to end this paragraph by underlying the extreme sensitivity of resonant diffraction to observe such a small amount of charge disproportionation.

A second important result, with straightforward implications in other CO compounds, is that the CO has very little influence on the (1, 0, 0) *forbidden* reflection whereas it is at the origin of the derivative line shape for the noninteger reflections. A charge disporportionation in the vicinity of the absorbing atom greatly affects the more localized orbitals, and thus both the $1s$ and the $3d$ energy levels will undergo an analogous shift. However the $4p$ states, less localized, are hardly affected.[23] Therefore the dipole-dipole contribution to the *K* edge of an atom experiencing a CO will be shifted towards higher or lower energies as compared to that found in the HT phase whereas the quadrupole preedges are little shifted during the oxidation processes. In a more general way, one has to proceed very cautiously on applying the derivative effect concept to *L* and *M* edges if the CO is expected to take place in *d* and *f* final states, respectively. We have computed the effect of the associated geometrical distortion onto the ASF and we have concluded that it remains negligible (± 0.1 eV) as compared to the observed energy shift and to the effect of the charge disproportionation ($\delta E = \pm 0.8$ eV). A first-order Taylor expansion of the scattering factor is justified by the small value of δE. It reads as $f^{+\delta} \approx f + \partial f/\partial E\, \delta E$ and $f^{-\delta} \approx f - \partial f/\partial E\, \delta E$, where f, $f^{+\delta}$, and $f^{-\delta}$ are the ASF tensors for the vanadium atoms with the HT

charge, and the $+\delta$ and $-\delta$ charge disproportionation, respectively. The derivative effect condition is best achieved for diffraction wave vectors with direction and amplitude such that the putative disproportionated vanadium ASF subtract. Conversely, for the *forbidden* reflections—such as (1, 0, 0)—the derivative term remains negligible in front of the combination of the ASF tensors weighted by its phase factors, and the sum of phase factors of V atoms of a given charge state almost cancels out.

By using the multiple-scattering theory we have checked that, except for the energy shift, the ASF is very little modified through the transition. Therefore our assumption above is plainly justified and we use energy shifted HT ASF in the LT structure. It can also be noticed that the XANES spectra show little sensitivity to the charge occupancy. The reason is exactly the same as the nonsensitivity of the (1, 0, 0) reflection: XANES adds the contributions of the different atoms, the small shifts due to the CO remain smeared within the experimental resolution. To finish this section, comparing with recent results on manganites,[24] it has been shown that in this case, the CO takes place by trapping electrons within pairs of Mn in a form that is known as Zener polaron. This kind of object will not give any signal in our resonant-scattering spectra.

IV. CONCLUSION

We have shown that a charge-ordering transition model quantitatively explains the resonant-scattering experiments in NaV_2O_5. The method presented here has the advantage to allow for a direct evaluation of the actual ordered charge disproportionation in the $3d$-transition-metal oxides. The charge ordering concerns a small fraction of an electron, mainly the *d*-orbitals, even if a contribution of the *s* orbitals cannot be excluded from the present study. This conclusion, although heavily suspected from the results of other works, points to reconsider electronic interactions in strongly correlated electron systems and to the role of small lattice distortions in accommodating extra charges. Finally with respect to compounds such as magnetite, where resonant diffraction experiments have yielded no sign of CO, we suspect that the studied diffraction peaks are hardly sensitive to an actual CO. Our results in NaV_2O_5 give evidence that spectroscopic effects associated to a very small CO are not at all negligible and that they should be observable in resonant diffraction experiments if convenient meaningful peaks are measured and the results contrasted with the help of appropriate simulations codes.

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