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X-ray anomalous scattering investigation of $BaVS_3$

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The quasi-one-dimensional conductor $BaVS_3$ undergoes a metal-insulator transition at $T_{MI}=70$ K accompanied by a formation of superstructure doubling the chain periodicity and a magnetic transition at $T_X=30$ K. We present an anomalous x-ray scattering investigation of the charge-density wave (CDW) satellite reflections at the V K-edge. Our study shows that no charge disproportionation larger than 0.01 electron occurs at T_{MI} and T_X. We interpret this result by the stabilization of two out-of phase CDW's for the d_{z^2} and $e(t_{2g})$ electrons, which induces an orbital ordering while reducing the intrachain Coulomb repulsions.

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Low-dimensional strongly correlated electronic systems exhibit very interesting phenomena like superconductivity, Mott localization, antiferromagnetism, and charge and spin density waves[1] (CDW and SDW). Moreover, the coupling of the electronic and magnetic instabilities with the lattice can stabilize charge ordering (CO or site CDW), bond order wave[2] (BOW), or orbital ordering. While structural refinement can provide a considerable amount of information, direct measurement of the charge or orbital component often provides unique additional information necessary to describe the ground-state symmetry. In this context, the study of the CO expected in the low-temperature CDW phase of the puzzling $BaVS_3$ system is very important. This system is especially interesting because it exhibits spin, charge, and orbital degrees of freedom and strong electronic correlations evidenced by a Luttinger-liquid behavior deduced from photoemission measurements.[1]

$BaVS_3$ has a quasi-one-dimensional (quasi-1D) structure made of chains of face-sharing VS_6 octahedra separated by Ba atoms.[3] At room temperature it crystallizes in the hexagonal space group $P6_3/\text{mmc}$ (Ref. 3) with two formula units per unit cell. It presents an original electronic structure:[4] the crystal field splits the $3d$ t_{2g} atomic levels into a d_{z^2} level giving rise to a broad quasi-1D band responsible for the metallic character of $BaVS_3$ and two quasidegenerate $e(t_{2g})$ levels (E_g^1 and E_g^2 below) giving rise to nearly nondispersive bands. With one $3d$ electron per V^{4+} atom and two V^{4+} per unit cell, there are two electrons to share between these bands. Local density approximation (LDA) band structure calculations give a nearly complete d_{z^2} band filling.[4] This result has been contradicted by recent structural[5] and angle-resolved photo emission spectroscopy[6] (ARPES) measurements which have motivated LDA+DMFT (local density approximation+dynamical mean-field theory) electronic structure calculations including the intra-atomic U and J Coulomb repulsions and notably the Hund's couplings. The calculations[7] show a redistribution of the occupancy of the d_{z^2} orbitals in favor of the localized $e(t_{2g})$. The d_{z^2} band tends to be half filled, leaving one electron to place in the two quasidegenerate quarter-filled E_g^i $(i=1,2)$ levels.

At $T_S=240$ K, $BaVS_3$ undergoes a second-order structural transition, leading to a zigzag arrangement of the V chains. This lowers the symmetry to the orthorhombic $Cmc2_1$ space group.[8]

At $T_{MI}=70$ K a metal-insulator transition[1] associated with a sharp maximum of magnetic susceptibility, specific heat[9] and lattice[10] anomalies are observed.

Below T_{MI} a superstructure is stabilized at the reduced wave vector $(1\ 0\ 1/2)_O$ (Ref. 5 and 11) (in the orthorhombic setting). It is announced by a quasi-1D regime of structural fluctuations detected up to 170 K (Ref. 5) where an excess of specific heat is also observed.[9] The T_{MI} transition has been attributed to a Peierls-like transition stabilizing a $2k_F$ CDW of the d_{z^2} electrons with $2k_F(d_{z^2})=0.5c_H^*$, a value which is in good agreement with the LDA+DMFT calculations.[7] This finding corresponds to half filling $[2\times 2k_F(d_{z^2})/c_H^*=1$ electron$]$ of the d_{z^2} band. This leaves one electron per unit cell for the two quasidegenerate $e(t_{2g})$ levels which explains the Curie constant value corresponding to one 1/2 localized spin every other V^{4+} (Ref. 5). A recent synchrotron x-ray powder diffraction refinement shows that below T_{MI}, the structure becomes monoclinic with space group Im and four inequivalent V atoms per unit cell.[8] The structural distortion corresponds to a tetramerization of the V^{4+} zigzag chain, setting a $2k_F$ BOW characterized by a modulation of the V-V bond lengths as represented in Fig. 1(a).

At $T_X=30$ K, a magnetic transition, involving one spin 1/2 out of two V, is evidenced by muon spin resonance (μSR), NMR, and neutron scattering.[1,12] In addition, a recent structural study[8] has suggested a possible CO below T_X. Indeed, at 5 K, on the basis of an empirical analysis using the bond valence sum (BVS) method, the charge of the V atoms has been estimated as 3.83, 4.14, 4.31, and 4.13, respectively for the V1, V2, V3, and V4 atoms. With respect to an average charge close to 4+, this corresponds to a charge modu-

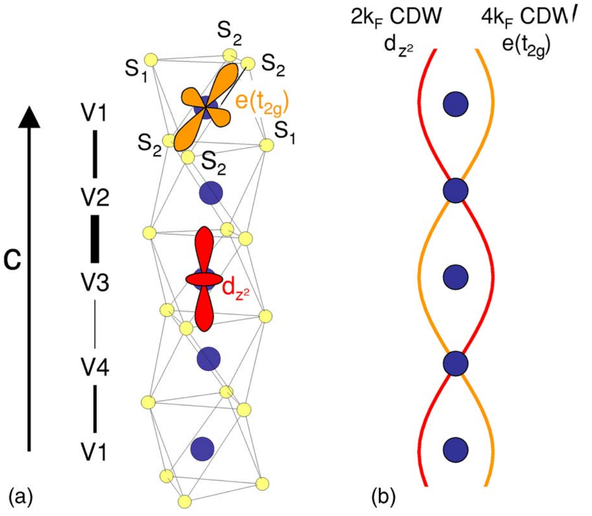

FIG. 1. (Color online) (a) The V chain with the four inequivalent V and bond lengths of the *Im* unit cell. (b) Out-of-phase CDW's of the d_{z^2} and the $e(t_{2g})$ electrons leading to the orbital ordering shown in (a)

lation of the form −0.25, 0, +0.25, 0 electron from V1 to V4, respectively. However, the BVS method generally overestimates the charge disproportionation especially if, as in the present case, the environment of the transition metal is not symmetric. In order to check the magnitude of the charge modulation on the V sites, we have directly measured the CO using anomalous x-ray scattering at the V *K*-edge.

Anomalous x-ray scattering is a powerful tool to investigate the amplitude of the CO. It measures the scattered intensity as a function of the x-ray beam energy, *E*. The anomalous diffraction comes from virtual photon absorption and emission processes due to electronic transitions between core electronic levels and unoccupied states near the Fermi level of the resonant atom. In the present case, experiments have been carried out at the V *K*-edge and the electronic transitions are $1s \rightarrow 4s$ via dipole-dipole processes and $1s \rightarrow 3d$ via quadrupole-quadrupole processes. Both processes are sensitive to the charge on the V site. In the case of a charge disproportionation, as the position of the edge is directly proportional to the number of electrons of the resonant atom, the anomalous scattering factors (f) of the different species (for instance, V^{4+x} and V^{4-x}) will be globally shifted in energy in such a way that $f^{4+x}(E+2x\, de/dx)=f^{4-x}(E)$, where e is the energy of the $1s$ level. Thus the intensity of the Bragg reflections involving the subtraction of the scattering factor of the two differently charged species will be proportional to $(\partial f/\partial E)^2$ and be very sensitive to x.[13] This is in particular the case for superstructure reflections arising from the metal-insulator (MI) transition and inducing an out-of-phase condition between V atoms of the unit cell (sinusoidal modulation of displacements). Anomalous scattering experiments performed at the *K*-edge are, however, not well suited to study the $3d$ orbitals as the $3d$ levels are directly probed only through the weak quadrupole-quadrupole processes whereas dipole-dipole processes probe indirectly these orbitals via their hybridization with the $4p$ orbitals of the S atoms.

Experiments were performed at the CRG beamline (D2AM) and at the ID20 beamline of the European Synchrotron Radiation Facility (Grenoble, France). A single crystal of $BaVS_3$ of about $0.1\times0.2\times2$ mm^3 was mounted on a four-circle diffractometer in a close-cycle He Displex refrigerator operating from 300 to 16 K. Sample preparation is described elsewhere.[8] The x-ray beam wavelength was selected by a Si(111) double-crystal monochromator with an energy resolution of 0.8 eV at the photon energies of the experiment. The incident beam was polarized perpendicular to the scattering plane (vertical) but no polarization analysis of the scattered beam was performed. The fluorescence spectrum has been systematically recorded for absorption corrections. Data were collected near the vanadium *K*-edge (5472 eV), typically between 5450 and 5500 eV with steps of 0.5 eV. The fluorescence background was removed to a negligible level by closing the slits.

Nine satellite reflections have been collected. Three of them, expected to be particularly sensitive to CO, have been carefully studied: $(1\ 4\ 1)_M$, $(0\ 1\ 3)_M$, and $(1\ 2\ 3)_M$ [the Miller indices are given in the monoclinic setting which corresponds in the orthorhombic setting to reflexions $\left(1\ 4\ \frac{1}{2}\right)_O$ $\left(0\ 1\ \frac{3}{2}\right)_O$, $\left(1\ 2\ \frac{3}{2}\right)_O$]. Moreover, for these reflections, the angle between the beam polarization and the vanadium chain is very different which allows us to investigate the influence of polarization. For the $(1\ 4\ 1)_M$ satellite reflection, the thermal variation of the anomalous scattering intensity was studied from 60 to 16 K. For the other reflections the working temperature was 16 K.

In anomalous scattering experiments, the raw data must be corrected for absorption. This is particularly necessary for $BaVS_3$ as the V *K*-edge is located between two Ba *L*-edges: L_3 at $\approx$5247 eV and L_2 at $\approx$5623 eV. Usually, the absorption corrections are obtained by multiplying the raw spectra by the fluorescence spectrum. This correction applies to integrated-intensity energy scans. However, for peak intensity energy scans, corrections apply slightly differently and the energy variation of the refractive index and of the attenuation length cannot be neglected.[14] Several procedures have been tested to account for these effects. The first one consists in dividing the raw data by the spectrum of a Bragg reflection near the satellite reflection for which the V contribution is weak, as the $(1\ 1\ 2)_M$ Bragg reflection in our case. A second procedure consists in multiplying the raw data by the square of the fluorescence spectra, following an empirical method. We have adopted the first procedure which gives more reliable results for the three studied reflections.

The fluorescence spectra recorded for the three sample orientations associated with the three satellite reflections are similar, and therefore the anomalous contribution is independent of the orientation between the V-chain axis and the beam polarization. This can be explained by the highly isotropic octahedral environment of the V atoms and by the almost identical V-S bond lengths in the $BaVS_3$ structure.[8] This also indicates that the charge distribution on the V is quasi-isotropic.

The corrected experimental intensity $I(E)$ of the $(1\ 4\ 1)_M$ satellite reflection at 16 K is presented in Fig. 2. It shows typical x-ray absorption near-edge structure (XANES) features. A major effect is seen at the V *K*-edge at 5472 eV. A

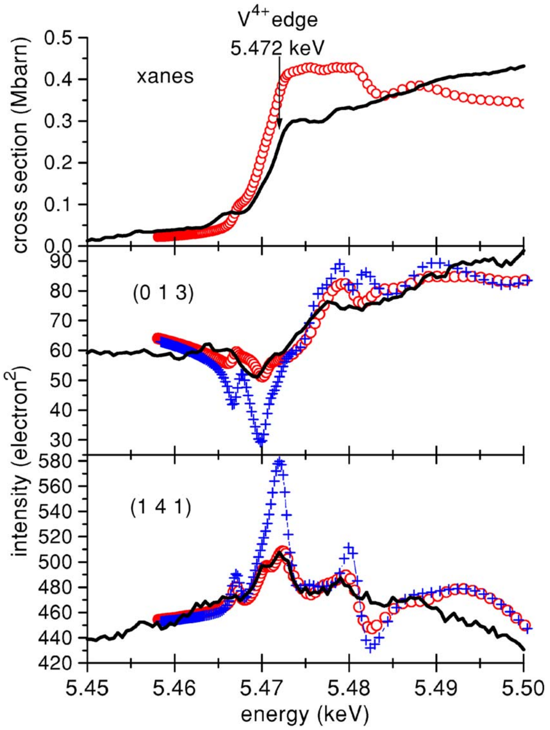

FIG. 2. (Color online) Energy variation of XANES and $I(E)$ of the $(1\ 4\ 1)_M$ and $(0\ 1\ 3)_M$ satellite reflections at 16 K. The solid line corresponds to the experiment. The calculated spectra for the optimum fit with $x=0\ e^-$ (circle) and $x=0.03\ e^-$ (cross) are shown.

very weak prepeak effect is also seen at an energy of 7 eV lower and is shown by calculations to be essentially due to dipole-dipole processes. The strong contribution at the edge is similar to the derivative effect expected for charge disproportion. However, this has to be checked by a calculation of the anomalous intensity. No substantial thermal variation of $I(E)$ was detected between 16 and 60 K.

$I(E)$ has been calculated using the FDMNES code,[15] which is efficient in the simulation of spin, orbital, charge, or geometrical ordering phenomena. The purpose of the present paper is the fit of the charge disproportionation, the unique fit parameters being the $3d$ V occupancy rates. The atomic structure used was the Im one at 5 K.[8] From these parameters, the total electron density is calculated, which determines the potential. Finally the Dyson or Dirac equations are solved to get the scattering factors. Convergence is reached with very big clusters up to 8.2 Å around the absorbing atoms, which includes about 108 atoms. This forbids the use of finite-difference methods, more precise but too time consuming, and consequently we use the full multiple-scattering theory under the muffin-tin approximation. Comparison with experiment is performed with the help of objective reliability factors.

The most important result is that no appreciable CO was found. $I(E)$ is very sensitive to the magnitude of the CO, and thus the best agreement remains remarkably close to a disproportionation equal to zero (Fig. 2). The use of different charge patterns on the V atoms always brings one to the same conclusion. For instance, using a $1-x$, 1, $1+x$, 1, CO pattern for the $3d$ electrons on, respectively, V1–V4, the best agreement is found for $x=-0.005$ (0.01). To illustrate the sensitivity, Fig. 2 shows that the calculated spectra for $x=0.03$ electron do not account for the data around 5.47 keV. The error bar of 0.01 electron has been estimated using the statistic repartition of the results over the three satellite reflections studied.

Figure 2 shows that the absolute intensity and the magnitude of the anomalous part (5% of the total intensity) are very well accounted for by the calculation with $x=0$ electron. The main features between 5470 and 5480 eV are very well reproduced, including details of their shape.

Our study shows that no sizable charge disproportionation ($x \geq 0.01$ electron) occurs in BaVS$_3$ below T_{MI} and T_X, in contrast with the suggestion in Ref. 11. Thus, the T_X transition seems to be mainly magnetic. As a comparison, it is worth noting that no evidence for entire CO modulation associated with electronic or spin orderings has been observed so far in oxides and in particular in Fe$_3$O$_4$. A weak amplitude of 0.04 electron has been experimentally detected at the CO–Spin-Peierls transition of NaV$_2$O$_5$.[13]

The experimental evidence of the absence of charge disproportionation on the V site associated with the tetramerization of the V chain in BaVS$_3$ is surprising because one generally expects a modulation of the electronic density in phase quadrature with the BOW modulation of the V-V distances. A possible explanation relies on the presence of two electronic subsystems based on the d_{z^2} and $e(t_{2g})$ electrons, respectively, which will arrange themselves in order to minimize the intrachain Coulomb repulsions. In this respect, two identical out-of-phase modulations could be stabilized at T_{MI} as schematically shown in Fig. 1(b). If the first one corresponds to the $2k_F$ CDW of the d_{z^2} electrons $[\rho(2k_F,d_{z^2})]$, the second one could correspond to a $2c_H$ modulation of the electronic density of each quarter-filled E_g^i orbital which can be identified as a $4k_F$ CDW $[\rho(4k_F,E_g)]$. The sum of the two sub-CDW gives the charge modulation: $\rho_c=\rho(2k_F,d_{z^2})+\rho(4k_F,E_g)\leqslant 0.01$ electron, which is null within the experimental errors. The difference of the two sub-CDW describes an orbital order: $\rho_{orb}=\rho(2k_F,d_{z^2})-\rho(4k_F,E_g)$, modulated with the $2c_H$ periodicity. Figure 1(b) represents the simplest case of two sinusoidal modulations, but a modulation of a more general shape is expected, because the CDW exhibits a second-harmonic modulation.[5] It is important to note that due to the localized character of the $e(t_{2g})$ electrons, the $4k_F$ CDW is probably not driven by a conventional 1D $4k_F$ instability. It could be more likely caused by an RKKY-like Coulomb coupling between E_g^i electrons via the $2k_F$ modulation of the d_{z^2} electrons. This mechanism should impose a $2c_H$ period for the E_g^i electrons, setting the $4k_F$ CDW. This induces their charge localization at T_{MI} but leaves available the E_g^i spin degrees of freedom for the T_X transition.

This scenario is supported by a qualitative analysis of the VS$_6$ octahedron distortions obtained from the structural refinement of the monoclinic phase of BaVS$_3$.[8] Figure 1 shows that the V d_{z^2} orbital points toward the triangular faces (S$_f$) perpendicular to the chain direction and that the E_g^1 orbital is located in the S$_2$ plane (the E_g^2 orbital points toward the apical S$_1$). Table I gives the difference of distances $[\Delta d(V-S)]$ between the V$_i$ and the S$_1$, S$_2$, and S$_f$. In such a

TABLE I. Difference of distance between V and selected S atoms of the VS_6 octahedra in the hexagonal (H), orthorhombic (O), and monoclinic (M) phases, according to the structural refinement of Ref. 8. See Fig. 1 for the definition of S_i and V_i.

			M			
Phase	H	O	V1	V2	V3	V4
$\Delta d(V-S_1)$ (Å)	0	0.40	0.47	0.53	0.37	0.50
$\Delta d(V-S_2)$ (Å)	0	0.10	0.02	0.08	0.13	0.08
$\Delta d(V-S_f)$ (Å)	0	0.07	0.14	0.12	0.04	0.10

case, the orbital of lowest energy is the one which has the most symmetric environment.[16] From inspection of the $\Delta d(V-S_2)$ distances, the E_g^1 orbitals are preferentially located on V_1 and less present on V_3. The opposite occupancy of the d_{z^2} orbital can be deduced from the inspection of the $\Delta d(V-S_f)$ distances. No clear statement concerning the occupancy of the E_g^2 orbital can be obtained from inspection of the $\Delta d(V-S_1)$ distances. Nevertheless, it appears from this qualitative analysis that there is an out-of-phase modulation of the occupancy of the V sites by the d_{z^2} and E_g^1 orbitals below T_{MI} as shown in Fig. 1.

Our experiment shows the absence of CO at the T_{MI} transition and sets new constraints on the theoretical models for $BaVS_3$. The scenario proposed to explain this result involves an orbital ordering. A direct experimental determination of this orbital ordering could only be obtained using an anomalous x-ray scattering study at the V *L*-edge.

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