Electronic structure of magnetic molecules \( \text{V}_{15} \): LDA+U calculations, X-ray emission and photoelectron spectra

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Electronic structure of \( \text{V}_{15} \) magnetic molecules (K\(_6\)[\( \text{V}_{15}\text{As}_6\text{O}_{42}(\text{H}_2\text{O})\])·8H\(_2\text{O} \)) has been studied using LSDA+U band structure calculations, and measurements of X-ray photoelectron (valence band, core levels) and X-ray fluorescence spectra (vanadium K\(_\beta\) and oxygen K\(_\alpha\)). Experiments confirm that vanadium ions are tetravalent in \( \text{V}_{15} \), and their local atomic structure is close to that of CaV\(_3\)O\(_7\). Comparison of experimental data with the results of electronic structure calculations show that the LSDA+U method provides a description of the electronic structure of \( \text{V}_{15} \) which agrees well with experiments.

PACS numbers: 75.50.Xx, 75.30.Et, 71.20.-b

Introduction

A new class of magnetic compounds, molecular magnets, have attracted much attention due to their unusual magnetic properties that in general are associated with mesoscopic-scale magnetic particles. These materials are the objects of studies for spin relaxation in nanomagnets, quantum tunneling of magnetization, topological quantum phase interference, quantum coherence, etc. In this work, we study the polyoxovanadate K\(_6\)[\( \text{V}_{15}\text{As}_6\text{O}_{42}(\text{H}_2\text{O})\])·8H\(_2\text{O} \) molecules (denoted below as \( \text{V}_{15} \)), which possess an interesting layered structure. This molecule contains fifteen antiferromagnetically coupled vanadium ions, each having spin \( S = 1/2 \), see Fig. 1. In contrast with many other molecular ferrimagnets (such as Mn\(_{12}\) or Fe\(_{12}\)), \( \text{V}_{15} \) is a molecular antiferromagnet with small net uncompensated spin 1/2, and it exhibits weak anisotropy. It presents unusual features, such as “butterfly-like” hysteresis loops, and, as theoretical estimates suggest, might exhibit rather long decoherence time. Previous considerations\textsuperscript{14,22} advocate that vanadium ions in this compound have valency of 4+. However, experimental studies elucidating the electronic structure of \( \text{V}_{15} \) are absent. Such studies are important for theoretical considerations of this complex compound, and firm experimental evidence of the tetravalent nature of vanadium ions in \( \text{V}_{15} \) is crucial.

We have addressed these issues by investigating \( \text{V}_{15} \) with X-ray photoelectron (XPS) and X-ray emission (XES) spectroscopies. These techniques allow determination of the charge (valence) state of the ions, provide information about the total density of states (DOS) normalized to photoionization cross-sections and the partial DOS of atomic components in the valence band, indicate variations in chemical bonding character, etc. We present the complete XPS and XES study of valence states of the V ions, and the distribution of the total and partial DOS in the valence band of \( \text{V}_{15} \). The experimental data obtained are compared with theoretical LSDA and LSDA+U calculations, and we show that the results obtained using LSDA+U technique agree well with experiments.

I. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The XPS measurements have been carried out using a PHI 5600ci multi-technique spectrometer using monochromatized Al K\(_\alpha\) radiation (\( E_{\text{exc}} = 1486.6 \) eV). Estimated energy resolution is 0.35 eV, and the base pressure in the vacuum chamber during measurements is about 5·10\(^{-9}\) Torr.

The XES V K\(_\beta\)\(_\text{s}\) spectra (\( 4p \to 1s \) transition) were measured using a fluorescent Johan-type vacuum spectrometer with a position-sensitive detector.\textsuperscript{24} Cu K\(_\alpha\) X-ray radiation from the sealed X-ray tube has been used for excitation of the V K\(_\beta\)\(_\text{s}\) XES. A quartz crystal (rhombohedral plane, second-order reflection) curved to \( R = 1.8 \) m was used as an analyzer. The spectra were measured with an instrumental energy resolution 0.22 eV. The vanadium L\(_{2,3}\) (\( 3d4s \to 2p_{1/2,3/2,5/2} \) transitions) and oxygen K\(_\alpha\) (\( 2p \to 1s \) transition) XES have been recorded at the Advanced Light Source (Beamline 8.0) employing the soft X-ray fluorescence endstation.\textsuperscript{25} The vanadium L\(_{2,3}\) and oxygen K\(_\alpha\) XES have been measured resonantly, through the V L\(_{2,3}\) and O K-edges, and
FIG. 1: (a) Structure of the \([\text{K}_6\text{V}_{15}\text{As}_6\text{O}_{42}(\text{H}_2\text{O})]^{6-}\) cluster, the large light-grey circles denote the vanadium ions. The central triangle containing the V3 ions is shaded. (b) The schematic sketch of arrangement of the vanadium ions in V15, and the proposed spin ordering.

non-resonantly (far from the threshold). The instrumental energy resolution of the V L and O K spectra is about 0.8 and 0.3 eV, respectively. The V 2p and O 1s X-ray absorption spectra have been measured in the total electron yield (TEY) mode. The total resolution of XES measurements is composed of the instrumental resolution (the values given above), and the width of the core level which depends on the lifetime of the hole. For vanadium K\(\beta_3\) XES, the width of the core level is about 0.79 eV, which gives about 1.0 eV of total energy resolution. For vanadium L emission, the core level width is about 0.8 eV, and for O Kα XES, the core level width is about 0.2–0.3 eV.

The single crystal of \([\text{K}_6\text{V}_{15}\text{As}_6\text{O}_{42}(\text{H}_2\text{O})]^{6-}\) was prepared as described in Ref. 6. It has a trigonal symmetry (space group \(R3c\)), as shown in Fig. 1b. The overall structure consists of three sets of non-equivalent vanadium atoms V1, V2, and V3. V1 and V2 belong to two nonplanar hexagons separated by a triangle of V3 centers forming the “layer structure” (Fig. 1b).

II. DISCUSSION OF EXPERIMENTAL RESULTS

The X-ray emission valence spectra originate from the electron transitions between the valence band and the core hole. The wave functions of the core states are strongly localized, and the angular momentum symmetry of the core electrons is well defined. Thus, according to the dipole selection rules, these spectra reflect the site-projected, and symmetry restricted partial densities of states (DOS). However, it is rather difficult to extract information about the occupied V 3d states from non-resonant V L\(_{2,3}\) XES because V L\(_3\) (3d4s → 2p\(_{3/2}\)) and V L\(_2\) (3d4s → 2p\(_{1/2}\)) transitions are strongly overlapped due to the small spin-orbital splitting of V 2p states (7.7 eV). To overcome this difficulty, we have used resonant excitation of V L\(_{2,3}\) XES, where the energy of incoming photons was tuned near V 2p-thresholds, and in this way we could selectively excite V L\(_3\) XES.

Fig. 2 shows the results of measurements of V L\(_{2,3}\) XES resonantly excited near the V 2p-thresholds. The excitation energies were selected in accordance with the features (a–f) on V 2p TEY (upper panel of Fig. 2), and indicated by vertical lines on V L-emission spectra (lower panel of Fig. 2). These energies exactly correspond to the energy of the elastic peaks which probe the unoccupied states, and the resulting intensities follow the absorption cross section. As one can see, the selectively excited V L\(_3\) XES (curves a and b, Fig. 2) reveal two peaks at 510.0 eV, and at 513.8–514.4 eV, which reproduce the structure of the undistorted distribution of V 3d states in the valence band, and can be related to O 2p and V 3d bands, respectively. The V 3d-like peaks have different emission energies (513.8 and 514.4 eV), which can be attributed to the contributions of non-equivalent vanadium atoms in the crystal structure of \([\text{K}_6\text{V}_{15}\text{As}_6\text{O}_{42}(\text{H}_2\text{O})]^{6-}\) (Fig. 1). The ratio of V 3d and O 2p (V 3d)-like peaks is higher for the curve a than for the curve b, which allows us to associate the peak at 513.8 eV with the contributions of V1 and V2 atoms from hexagons (we denote this contribution as 1-2), and the peak at 514.4 eV — with the contribution of V3 atoms.
FIG. 3: Excitation energy dependence of O Kα XES of V$_{15}$

(we denote this contribution as 3). At higher excitation energies, the peaks at 513.8–514.4 eV are strongly overlapped with the main peak of V L$_2$ XES (curves e–f, Fig. 2), which makes it very difficult to establish their location and width.

The resonantly excited O Kα XES of V$_{15}$ (Fig. 3) reveal significant changes in the fine structure, depending on excitation energy. These changes can be explained by contributions of different oxygens belonging to the polyoxovanadate part and the water of hydration in the V$_{15}$ structure, which are selectively excited by tuning the energy of incoming photons. Using the X-ray fluorescence measurements of liquid water, we can attribute the feature e of O 1s TEY (upper panel, Fig. 3) and corresponding O Kα XES (curve e, lower panel, Fig. 3) to the oxygens belonging to the water of hydration. We believe that the curve d of O Kα XES (lower panel, Fig. 3) corresponds to the contribution of oxygen atoms from the polyoxovanadate part of V$_{15}$.

In Fig. 4, we compare the XPS VB and X-ray emission spectra for V Kβ$_5$, V L$_3$, and O Kα XES. To convert the X-ray emission spectra to the binding energy scale, we have used XPS binding energies of core levels (V 2p$_{3/2}$, O 1s), emission energy of V Kα$_1$ (2p$_{3/2}$ → 1s transition), V L$_3$ (3d → 2p$_{3/2}$ transition) and O Kα (2p → 1s transition) measured for V$_{15}$. Such a comparison provides a direct interpretation of XPS VB (which probes total DOS), because the XES of the constituents probe partial DOS's due to the dipolar selection rule. As one can see, at the bottom of the valence band, the O 2s (∼22 eV) and K 3p states (∼18 eV) are located, as revealed in the XPS VB. V Kβ$_5$ XES also consist of an energy band (Kβ''$_3$) around 21 eV, because of the hybridization between V 4p and O 2p states. Such hybridization is typical for all vanadium oxides. According to Fig. 4, in the middle of the valence band V 3d (V 4p) and O 2p states are concentrated, and strong mixing is present. Our spectra demonstrate that at the top of the valence band, the V 3d states prevail.

To analyze the oxidation state of V ions and their local atomic structure, we have compared V L$_3$ and V Kβ$_5$ XES of V$_{15}$ with the corresponding spectra of the reference samples VO$_2$ (where V ions have valency 4+), V$_2$O$_5$ (where V ions have valency 5+) and CaV$_3$O$_7$ (where V ions have valency 4+) (Figs. 5a,b). Fig. 5 shows that V Kβ$_5$ and V L$_3$ XES of V$_{15}$ are closer to those of VO$_2$ than to V$_2$O$_5$, which suggests that vanadium ions are tetravalent in V$_{15}$. We need to point out that the relative intensity of elastic peak with respect to the main peak of the L spectrum of V$_{15}$ is much higher than that of VO$_2$ (Fig. 5a), although the vanadium ion has the same oxidation state (4+) in both compounds. The elastic peak
corresponds to the transitions from vacant $d$-states occupied by a photoelectron in the intermediate state of the absorption-emission process. We can assume that its high intensity indicates that the $d$-electrons in $V_{15}$ are more localized as a result of larger $V$–$V$ distances. Indeed, the average $V$–$V$ distance in $VO_2$ is about 2.62 Å, whereas in $V_{15}$ the distance $V1$–$V2$ is 2.86 Å and 3.063 Å. The $V3$–$V3$ distances (6.926 Å) in $V_{15}$ are even larger.

It is known that the spectral parameters of $V K_{\beta 5}$ XES (the energy position, the $K\beta''/K\beta_5$ intensity ratio) are very sensitive not only to the oxidation state of $V$ ions in compounds, but also to their nearest neighbors. Therefore, we have chosen $CaV_3O_7$ ($V^{4+}$ oxidation state) and $V_2O_5$ ($V^{5+}$ oxidation state) as the reference samples: in these compounds, as well as in $V_{15}$, vanadium atoms are situated inside a distorted pyramid made by five oxygen atoms. Comparison of the $V K_{\beta 5}$ spectra of $V_{15}$, $VO_2$, $V_2O_5$, and $CaV_3O_7$ (Fig. 5b) shows that the energy position, the $K\beta''/K\beta_5$ intensity ratio, and the spectrum shape of $V_{15}$ are practically identical to the spectrum of $CaV_3O_7$, but significantly differ from the $V_2O_5$ spectrum. This gives experimental confirmation that vanadium ions in $V_{15}$ have the oxidation state ($4+$) and the configuration of neighboring atoms is similar to that of $CaV_3O_7$.

To obtain deeper understanding of the electronic structure of $V_{15}$, and to compare the experimental data with theoretical predictions, we have performed a series of LSDA+U calculations. This method is known to provide a good theoretical description for most metal-oxide crystalline systems, since in most metal-oxide crystals the account of the on-site Coulomb repulsion (characterized by the value of the parameter $U$) is crucial for correct description of their properties. Moreover, this method has been successfully applied for the molecular magnet $Mn_{12}$, and account of the on-site Coulomb repulsion yields the correct value for the gap in the electronic spectrum. Therefore, we expect that the LSDA+U approach should also be successful in describing the electronic structure of $V_{15}$. As shown below, this is indeed the case. Details of application of the LSDA+U technique to electronic structure calculations of molecular magnets are described in Ref. 22.

To make the calculations feasible and reasonably precise, we have followed standard practice, excluding from consideration the molecules of water of hydration, but retaining completely the polyoxovanadate part of the $V_{15}$ molecule. The positions of constituent ions have been obtained from the X-ray data. The calculations presented below have been made for $J = 0.8$ eV and for $U = 4$ eV. The calculations for other values of $U$, from 3.8 eV to 5.4 eV, do not significantly change the DOS, but the distance between the bands increases with $U$.

We note that our calculations with $U = J = 0$ (which coincide with the ASA-LMTO LSDA approach) do not give correct results, exhibiting qualitatively erroneous
non-zero DOS at the Fermi level. As reported in Refs. 12,24, the use of LSDA approach with Gaussian basis and GGA functional, along with theoretical optimization of the structure of $V_{15}$ molecule, gives a gap between the occupied and non-occupied states, with zero DOS at the Fermi energy. As can be concluded from Ref. 24, this approach does not agree with some details present in XES spectra, e.g. the $O 2p$ and $V 3d$ bands are separated by larger interval than obtained experimentally, and than given by our LSDA+U calculations with $U = 4$ eV. The situation is not yet clear, further work is needed to clarify the details of the electronic structure of $V_{15}$, therefore we do not discuss this issue further here.

The calculated DOS of $d$, $p$, and $s$ electrons of inequivalent $V_1$, $V_2$, and $V_3$ ions are presented in Figs. 6,7,8, and the DOS of oxygen ions belonging to the polyoxovanadate part of the $V_{15}$ molecule are shown in Fig. 9. The total DOS of electrons in the $V_{15}$ molecule is presented in Fig. 10. Until now, detailed quantitative experimental information on the electronic structure of $V_{15}$ has been lacking, but the results of our calculations agree with available qualitative experimental facts. E.g., a finite gap ($\Delta E \sim 1$ eV) in the total DOS is correctly reproduced by the LSDA+U calculations. In this work, using the results of XES and XPS investigations described above, we can make quantitative comparison between theory and experiment.

The $d$ electrons of the vanadium ions determine the magnetic behavior of $V_{15}$. Previous magnetic measurement, and the results of XES/XPS studies presented above, confirm that $V$ ions are tetravalent, with the total spin $1/2$ per ion. Moreover, the measurements of dc spin susceptibility and EPR data suggest that the intra-molecular exchange interactions between $V_1$ and $V_2$ (belonging to the upper and lower hexagons) are strong, while the exchange with $V_3$ ions is much smaller.

These facts agree well with our theoretical results. The calculated 3$d$ DOS of all vanadium ions (see Fig. 6) demonstrate two pronounced features: the sharp peaks located at about $-1$ eV from the Fermi level for $V_1$ and $V_2$ (for $V_3$, about $-0.5$ eV), and the broad bands extended between $-2$ eV and $-7$ eV. The sharp peaks correspond to localized $V$ $d$-electrons responsible for formation of well-defined local spin $S = 1/2$ of vanadium ions. Our calculations, indeed, give the values of magnetic moments very close to $1\mu_B$, namely:

$$\mu = -0.94\mu_B \quad \text{for } V_1,$$

$$\mu = 0.91\mu_B \quad \text{for } V_2,$$

$$\mu = -1.0\mu_B \quad \text{for } V_3.$$  

The broad bands in the spectrum of $V$ $d$ electrons clearly demonstrate the signatures of hybridization between the $V$ $d$ and $s$ states, on one hand, and the $O$ $p$ states, on the other. The broad structure of $O$ $p$ DOS is reproduced in $V_1$ and $V_2$ $d$ and $s$ DOS, and, somewhat weaker, in $V_3$ $d$ and $s$ DOS. This is in agreement with the fact that magnetic superexchange interactions between $V_1$ and $V_2$ (located in upper and lower hexagons) are very strong ($\sim 800$ K, according to Ref. 7), and involve strong hybridization between $V$ $3d$ and $O$ $2p$ orbitals, while the interactions of $V_3$ (located in the central triangle) are much weaker, implying weaker hybridization. Similar hybridization signatures between $V$ $s$ orbitals and $O$ $p$ orbitals (see Figs. 8,9) correspond to chemical bonding of $V$ with surrounding oxygens.

The calculated DOS are in agreement with the results
of XES measurements. The two features of vanadium DOS’s, the sharp peaks and the broad bands, correspond to the two wide peaks, at about $-1.5$ eV and $-6$ eV clearly seen in the vanadium L₃ XES spectrum in Figs. 2, 4. In agreement with experimental data, the sharp “magnetic” peak in V3 is closer to the Fermi level, than the “magnetic” peaks of V1 and V2 (Fig. 2, 4). The difference between the peak widths and intensities in the calculated DOS and in the measured XES spectra can be attributed to the difference in matrix elements corresponding to different V d states. It is known that such a difference can be very large and it can lead to significant differences between the “bare” peak widths/heights in the DOS and the widths/intensities of corresponding peaks as observed in XES spectra. Therefore, following the common practice, we have restricted our discussion to the peak positions, rather than widths and heights. Furthermore, the structure of calculated V p states DOS is in good agreement with the XES spectra, Figs. 3, 4. The broad band extending between $-2$ eV and $-8$ eV is revealed in the V Kβ₅ XES spectra as a wide peak located in the same energy interval. Similarly, the calculated DOS for O p states (a broad band from $-2$ eV to $-8$ eV) exhibits itself as a broad feature in the O Kα XES spectra in the same energy range, see Figs. 3, 4.

The X-ray emission is a selective tool which probes only the states allowed by dipolar selection rules, but XPS probes the total density of states. The calculated total DOS (Fig. 10) exhibits a number of peaks and dips. But the XPS spectra, apparently, lacks sufficient energy resolution to see this fine structure, since the resolution of XPS measurements on dielectric crystals, such as V₁₅, is considerably reduced due to the charging effect. Therefore, the total DOS in the energy range of interest (between the Fermi level and $-8$ eV) is seen as a single hump of the shape similar to the smeared total DOS as obtained from LSDA+U calculations. This is in qualitative correspondence with the fact that the “magnetic” peaks in the V 3d states constitute only a small fraction of the total states in V₁₅. Along with the insufficient resolution, other reasons might reduce the intensity of “magnetic” peak, e.g. contamination of the surface (XPS, in contrast with XES, is surface-sensitive, and the peak seen in the bulk XES spectra, can be suppressed if the surface is spoiled), or the final state effects.

IV. SUMMARY

In this work, we have performed an extensive experimental and theoretical investigation of the electronic structure of V₁₅ magnetic molecules. Using XPS and XES spectroscopies, we have confirmed that vanadium ions are tetravalent, and their local atomic structure is close to that of CaV₃O₇. We have managed to separate, identify, and study in detail the contributions from inequivalent vanadium ions V1,2 (belonging to the upper and lower hexagons), and V3 (located in the triangle sandwiched between the hexagons) to the XES spectra. For theoretical studies, we have employed the LSDA+U approach with $U = 4$ eV, which results in agreement with the experimental data.

We found good agreement between the experimental data and the results of calculations. Our calculations also confirm the oxidation state 4+ of vanadium ions in V₁₅. The main features of the calculated DOS correspond to the peaks seen in XES and XPS spectra for V and O ions. High intensity of the elastic peak of V L₃ XES indicates the existence of localized states of V1, which are due to the peculiar crystal structure of V₁₅, where the V–V distances are much larger than the V–X ones. The calculated magnetic moments of V1, V2, and V3 are very close to $1\mu_B$, i.e. to the moment of a free V⁴⁺ ion, in contrast with other compounds of tetravalent vanadium.
Acknowledgments

Funding by the Russian Foundation for Basic Research (Projects 00-15-96575 and 02-02-16674), NATO Collaborative Linkage Grant (PST.CLG.978044), and the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. The work is partially supported by the Netherlands Organization for Scientific Research, NWO project 047-008-16. This work was partially carried out at the Ames Laboratory, which is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-82 and was supported by the Director of the Office of Science, Office of Basic Energy Research of the U. S. Department of Energy.

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