

## Electronic structure and exchange interactions in $V_{15}$ magnetic molecules: LDA+U results

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Single-molecule magnets  $V_{15}$  ( $K_6[V_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$ ) have attracted a great deal of attention recently. These magnets are promising systems for studying such fundamental problems as spin tunneling, spin coherence, and low-temperature spin relaxation. To understand in detail the internal magnetic and electronic structure, and the intramolecular interactions responsible for the formation and low-energy excitations in  $V_{15}$  molecules, we have performed electronic structure calculations using the local spin density approximation with on-site repulsion parameter  $U$  (so-called LSDA+U) approach. The calculated values of magnetic moments and charge states of vanadium ions agree well with experiments confirming the  $V^{4+}$  state of vanadium ions. We found that for  $U \sim 4-5$  eV, good description of known properties of  $V_{15}$  molecule can be achieved. Comparing the results of the band-structure calculations with the experiments, we have found that the LDA+U description of the  $V_{15}$  magnet is in agreement with experimental data. © 2003 American Institute of Physics. [DOI: 10.1063/1.1540035]

Recently, single-molecule magnets have attracted much attention.<sup>1,2</sup> These materials are promising systems for the studies of spin relaxation in nanomagnets, quantum tunneling of magnetization, topological quantum phase interference, quantum coherence, etc.<sup>3-5</sup> In particular, the polyoxovanadate  $K_6[V_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$  molecules (denoted below as  $V_{15}$ ) possess an interesting layered structure,<sup>6-8</sup> with 15 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  $Fe_8$ ),  $V_{15}$  is a molecular antiferromagnet with small uncompensated spin  $1/2$ , and exhibits weak anisotropy. It presents unusual features, such as “butterfly-like” hysteresis loops,<sup>9</sup> and, as theoretical estimates show,<sup>10</sup> might demonstrate rather long decoherence time.

The detailed theoretical study of the internal electronic and magnetic structure of  $V_{15}$  molecules is important for understanding of its unusual properties, and the electronic structure calculation is a valuable tool for such studies. Recently, *ab initio* calculations using the generalized gradient approximation (GGA) technique have been performed and

have provided an important information about the intramolecular structure of  $V_{15}$ .<sup>11,12</sup> However, the GGA technique neglects the electronic correlations caused by on-site Coulomb repulsion. In many metal-oxide crystals,<sup>14,15</sup> the account of this interaction is important for correct description of their properties, and it might also be the case for molecular magnets. To clarify the role of the on-site repulsion, we have undertaken investigation of  $V_{15}$  using the local spin density approximation with on-site repulsion parameter  $U$  (LSDA+U) method,<sup>13</sup> which takes the on-site repulsion into account via the parameter  $U$ . Below, we present the results of our calculations, and show that for  $U \sim 4-5$  eV, the results of the LSDA+U method agree with the experimental data.

The overall structure of  $V_{15}$  is quasispherical, with three sets of nonequivalent 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. 1). To calculate the electronic and magnetic intramolecular structure of  $V_{15}$ , we use the atomic sphere approximation linear muffin tin orbital LSDA+U method. This method has been successfully applied before<sup>16</sup> for the molecular magnet  $Mn_{12}$ , producing good agreement with experimental data.

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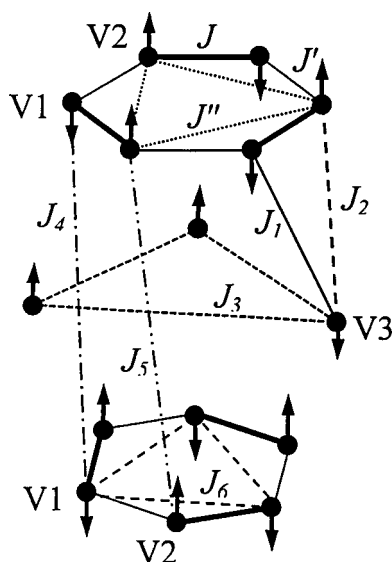


FIG. 1. Sketch of arrangement of vanadium ions in the  $V_{15}$  molecule. The arrows schematically show the ground-state spin ordering.

Therefore, we expect that the LSDA+ $U$  approach might also be useful in the case of  $V_{15}$ . The details of the application of the LSDA+ $U$  technique to electronic structure calculations of molecular magnets are described in Ref. 16. To make the calculations feasible and reasonably precise, we have followed standard practice,<sup>16,17</sup> excluding from consideration the crystal water molecules, but retaining completely the polyoxovanadate part of the  $V_{15}$  molecule. The calculations presented below have been made for  $U=4-5.2$  eV, the values typical for the vanadium-oxide crystal systems.

The calculated density of states (DOS) of the vanadium  $d$  electrons and for the oxygen  $p$  electrons are presented in Figs. 2 and 3, correspondingly. These figures correspond to  $J=0.8$  eV and  $U=4$  eV. For larger values of the on-site re-

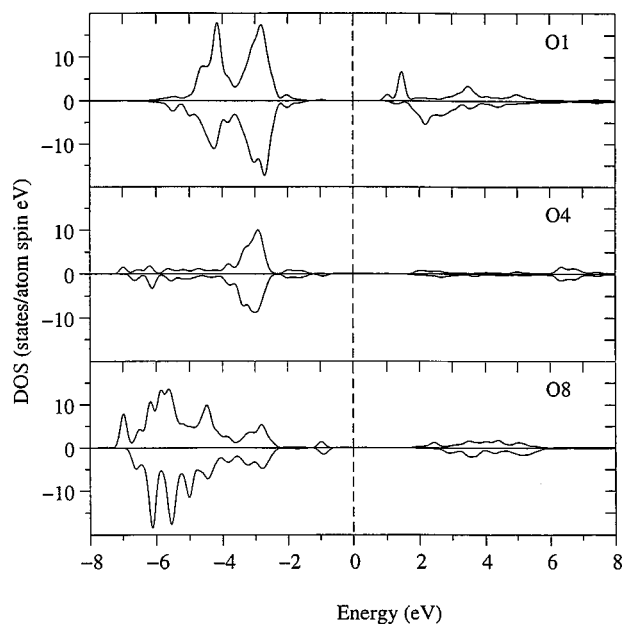
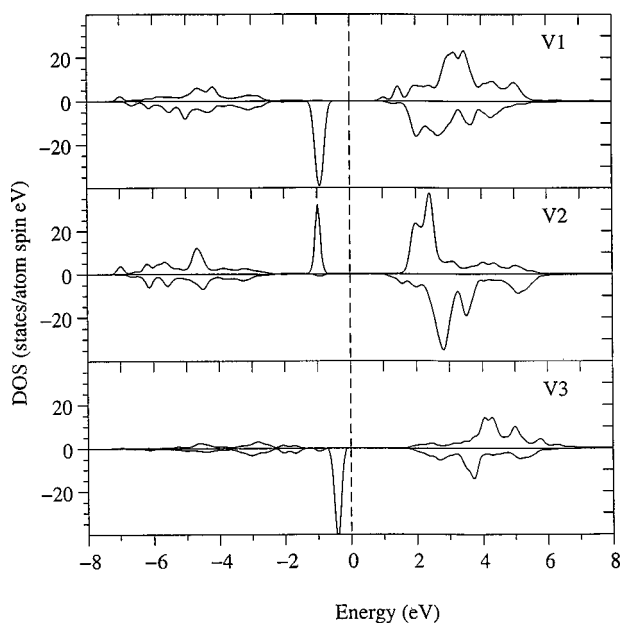


FIG. 2. DOS of  $d$  electrons of inequivalent V1, V2, and V3 ions. The DOS are calculated for  $U=4$  eV.

FIG. 3. Total DOS of  $p$  electrons of oxygens belonging to the polyoxovanadate part of  $V_{15}$  molecule. The DOS are calculated for  $U=4$  eV.

pulsion parameter  $U$ , the DOS do not significantly change, but the distance between the bands increases with  $U$ .

The  $d$  electrons of vanadium ions determine the magnetic behavior of  $V_{15}$ . Previous magnetic measurements,<sup>6-8</sup> confirm that V ions are tetravalent, with the well defined total spin  $1/2$  per ion. Moreover, the dc spin susceptibility and electron paramagnetic resonance data suggest that the intramolecular exchange interactions between the V1 and V2 ions (belonging to the upper and lower hexagons) are strong, while the exchange between the V3 ions is much smaller. These facts agree well with our theoretical results. The calculated  $3d$  DOS of all vanadium ions (see Fig. 2) demonstrate two pronounced features: the sharp peaks located at about  $-1$  eV from the Fermi level for V1 and V2 (for V3, about  $-0.5$  eV), and the broad bands extended between  $-2$  and  $-7$  eV. The sharp peaks correspond to localized V  $d$  electrons responsible for the formation of a 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  $\mu = -0.94\mu_B$  for V1,  $\mu = 0.91\mu_B$  for V2, and  $\mu = -1.0\mu_B$  for V3. The broad bands in the spectrum of V  $d$  electrons clearly demonstrate the signatures of hybridization between the V  $d$  and the oxygen  $p$  states. The broad structure of oxygen  $p$  states DOS is reproduced in V1 and V2  $d$  DOS, and, somewhat weaker, in V3  $d$  and  $s$  DOS. This is in agreement with the fact that magnetic superexchange interactions between V1 and V2 (located in upper and lower hexagons) are very strong ( $\sim 800$  K, according to Ref. 7), and involve strong hybridization between V  $3d$  and oxygen  $2p$  orbitals, while much weaker interactions of V3 ions imply weaker  $p-d$  hybridization.

To make a quantitative comparison with experiments, we have calculated the values of the gap in the electronic spectrum of  $V_{15}$ , and the intramolecular exchange interactions for  $J=0.8$  eV, and for different values of  $U$  (see Table I).

TABLE I. The values of exchange parameters (in Kelvin), gap in the electronic spectrum, and the distance  $\Delta E$  between the spin ground state and the first excited spin state for different values of  $U$ :  $U=4.2, 4.8, 5.0, 5.2,$  and  $5.4$  eV.

Atom1	Atom2		4.2	4.8	5.0	5.2	5.4
$V_1$	$V_2$	$J$	-889	-828	-809	-791	-772
$V_1$	$V_2$	$J'$	-42	-33	-30	-28	-25
$V_2$	$V_2$	$J''$	-131	-123	-120	-117	-114
$V_1$	$V_3$	$J_1$	-207	-177	-168	-160	-153
$V_2$	$V_3$	$J_2$	-131	-124	-122	-119	-117
$V_3$	$V_3$	$J_3$	-5	-4	-3	-3	-3
$V_1$	$V_1$	$J_4$	-13	-11	-11	-11	-10
$V_1$	$V_1$	$J_5$	-3	-3	-3	-3	-3
$V_2$	$V_2$	$J_6$	-3	-2	-2	-2	-2
gap (eV)			1.40	1.98	2.39	2.41	2.42
$\Delta E$ (K)			8.38	6.51	4.92	4.85	4.79

The value of the electronic gap can be estimated from the results of optical measurements. The data obtained in the group of Musfeldt<sup>18</sup> suggest the value of 1.2 eV for the energy of the vertical transitions. The magnitude 1.4 eV for the gap, corresponding to  $U=4.2$  eV, is close to the result of optical measurements, but other values of the gap can also be compatible with the experiment. To make rigorous comparison, more extensive calculations are needed, which take into account the values of matrix elements between different electron states. Corresponding work is now in progress.

Furthermore, using the calculated exchanges, we have performed exact diagonalization of the spin Hamiltonian of  $V_{15}$ . As a result, we obtain the energy difference  $\Delta E$  between the spin ground state and the first excited spin state. The experimental value  $\Delta E_{\text{exp}}=3.7$  K is known from magnetic measurements,<sup>9</sup> and from the neutron scattering experiments.<sup>19</sup> As one can see from Table I, the calculated values of  $\Delta E$  for  $U\sim 5$  eV are close to the experimental value. The difference of 20%–30% can be caused by the precision of calculation of the exchange (20%–30% is a typical precision of such calculations), or by omission of anisotropic interactions which are noticeable at this energy scale.<sup>9,10,19</sup> Also, using the exact diagonalization results, we have calculated the temperature dependence of the effective

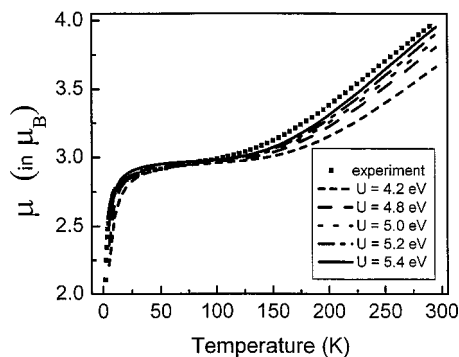


FIG. 4. Temperature dependence of the effective magnetic moment of the  $V_{15}$  molecule. The results calculated using the exchanges corresponding to different values of  $U$  are compared with the experimental data. The calculated curves corresponding to  $U$  close to 5.0 eV are close to the experimental curve.

magnetic moment of the molecule  $\mu(T)$ . The results of these calculations are presented in Fig. 4, along with the experimental data measured on a fresh-grown sample of  $V_{15}$ . Comparison of the calculated curves  $\mu(T)$  with the experimental one shows that the values of  $U$  close to 5 eV result in good agreement with the experimental data.

Summarizing, we have performed theoretical investigations of electronic structure of  $V_{15}$  magnetic molecules using LSDA+ $U$  electronic structure calculations. Our results agree with known experimental facts. The calculated magnetic moments of individual vanadium ions correspond to the well-localized spin 1/2 on vanadium sites. For the values  $U\sim 4-5$  eV of the on-site Coulomb repulsion parameter, a good description of  $V_{15}$  electronic and magnetic properties has been obtained. The values of the electronic gap are compatible with the results of optical measurements. Using the exchange couplings calculated for  $U\sim 4-5$  eV, we have diagonalized exactly the spin Hamiltonian of  $V_{15}$ . The energy of the first excited spin state agrees with the experimental value. The calculated temperature dependences of the molecule's effective magnetic moment  $\mu(T)$  are close to the experimental curve for the values of  $U$  close to 5 eV.

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