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

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Single-molecule magnets of the type $V_{15}(K_6[V_{15}As_6O_{42}(H_2O)]\cdot 8H_2O)$ have attracted a great deal of attention recently, being promising systems for studying low-temperature spin-relaxation and quantum-spin tunneling. 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 LSDA+U approach. The calculated values of magnetic moments and charge states of vanadium ions agree well with experiments, thus confirming the V^{4+} state of vanadium ions with a well-defined spin 1/2. We found that the account of the on-site Coulomb repulsion is important for correct description of V_{15} internal properties; in particular, for the values of the on-site repulsion parameter $U \sim 4$–5 eV, we can achieve good agreement with known properties of V_{15}, such as the temperature dependence of susceptibility, and the energies of the low-lying eigenstates of the spin Hamiltonian.

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INTRODUCTION

Recently, single-molecule magnets have attracted much attention.[1,2] These materials are promising systems for the studies of spin relaxation in nanomagnets, quantum tunneling of magnetization, topological quantum-phase interference, quantum coherence, etc.[3–5] In particular, polyoxovanadate $[V_{15}As_6O_{42}(H_2O)]^{6-}$ molecules (denoted below as V_{15}) possess an interesting layered structure,[6–8] 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 total spin 1/2, and exhibits weak anisotropy. It presents unusual features, such as "butterflylike" hysteresis loops,[9] and, as theoretical estimates show,[10] might demonstrate rather long decoherence time. In order to investigate complex collective phenomena observed in V_{15} crystals, it is necessary to understand in detail the internal electronic and magnetic properties of a single V_{15} molecule, and to use the knowledge gained as a basis for further research (e.g., for developing accurate models of low-energy excitations in V_{15} molecules). In this work, which constitutes an important step toward such understanding, we present a study of the internal electronic structure, magnetic ordering, and the intramolecular magnetic exchange interactions between the spins of vanadium atoms in V_{15} molecules.

Recently, *ab initio* electronic structure calculations using GGA (generalized gradient approximation) technique have been performed and have provided important information about the intramolecular structure of V_{15}.[11,12] However, the GGA technique neglects the electronic correlations caused by the Coulomb repulsion. In many metal-oxide crystals,[13–16] the account of this interaction is important for a correct description of their properties, which might be also the case for molecular magnets. In particular, the intramolecular exchange interactions for a V_{15} molecule, which were obtained in Refs. 11 and 12 without taking into account the Coulomb repulsion, had to be reduced by a factor of three in order to achieve agreement with experimental data. To elucidate the role of the on-site repulsion, we have undertaken investigation of V_{15} using the LSDA+U (local spin-density approximation plus U) method,[13] which takes into account the on-site Coulomb repulsion via the parameter U. In practice, full

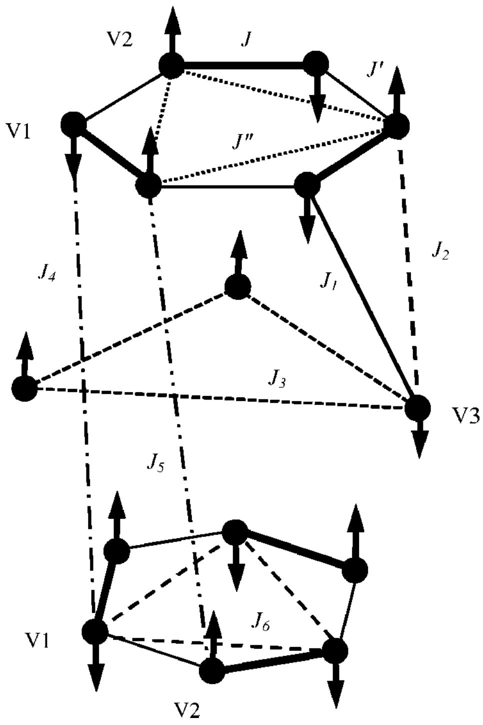

FIG. 1. The sketch of arrangement of vanadium ions in the V_{15} molecule. The arrows schematically denote the individual spins.

screened Coulomb matrix elements were included in the rotationally invariant LDA+U calculations.[14] The irreducible Slater parameters (the Coulomb repulsion parameter U and the Hund's intra-atomic exchange J) can be obtained in so-called constrained LSDA calculations.[13] Earlier, we have investigated the U-dependence of electronic structure and magnetic interactions in V_{15} system in order to check that the optimal LDA+U results correspond to reasonable values of U for vanadium oxide system,[13] keeping in mind that the parameter J is not very sensitive to different screening environment and is almost constant for all transition metal compounds.[13,14] Below, we show that an account of the Coulomb repulsion is important for V_{15} molecules, allowing quantitatively correct description of their properties. In particular, we demonstrate that for $U \sim 4-5$ eV, the results of LSDA+U method agree with the available experimental data.

The rest of the paper is organized as follows. In Sec. I, we describe the structure of the V_{15} molecule, and the details of the electronic structure calculations. In Sec. II, we present and discuss the results of the electronic structure calculations and diagonalization of the spin Hamiltonian. In Sec. III, we provide a brief summary of the results.

I. STRUCTURE OF THE MOLECULE AND THE METHOD OF CALCULATIONS

The overall structure of the V_{15} anion is quasispherical, with three sets of nonequivalent vanadium centers 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 make the calculations feasible and reasonably precise, we have followed standard practice,[18,19] excluding from consideration the crystal water molecules, but retaining the complete polyoxovanadate part of the V_{15} molecule.

The V_{15} molecules are arranged in a crystal. The ionic lattice of the crystalline V_{15} compound is modeled using periodic boundary conditions. For our calculations we reproduce the solid-state lattice of $K_6[V_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$ using the crystallographic asymmetric unit (the irreproducible part) of the V_{15} polyoxovanadate cluster unit and applying all symmetry operations of the compound's space group (R-3c). This procedure allows us to use the standard codes developed earlier for studying simpler crystalline solids. On the other hand, due to negligibly small overlap between the electron orbitals of different molecules in a crystal, the interpretation in terms of single-molecule properties remains valid.

To calculate the internal electronic and magnetic structure of V_{15}, we use the ASA-LMTO (Atomic Sphere Approximation–Linear Muffin-Tin Orbitals) LSDA+U method.[13] This method has been successfully applied before[18] for the molecular magnet Mn_{12}, producing good agreement with experimental data. Therefore, we expect that LSDA+U approach might also be useful in the case of V_{15}. For our calculations we used the Stuttgart TB-47 code.[17] The method we use is known to work very well for closely packed structures, while for more loose packing there is an ambiguity in choosing the atomic radii. Nevertheless, it appears that the structure of V_{15} is sufficiently closely packed, and there is not much room for varying the atomic radii (e.g., the radius of V atoms R_V can be varied from 1.1 Å to 1.6 Å, which is reasonable interval for R_V). Our calculations for different values of the atomic radii show that these variations leave the results practically unchanged. All the results presented below are obtained for $R_V=1.27$ Å and $R_O=1.05$ Å, $R_{As}=1.31$ Å, $R_K=2.21$ Å, where the latter three symbols denote the radii of oxygens, arsenics, and potassiums, respectively. These values give the overlap between atomic spheres close to 16 %, which is a standard value for the ASA-LMTO method. Furthermore, we used 184 empty spheres in order to fill the space between neighboring V_{15} molecules in the crystal. When choosing the locations and the radii of the empty spheres, we tried to minimize an overlap between empty spheres and atomic spheres. Actually, the choice of empty spheres is not very important for molecular magnets because a few layers of empty spheres separate neighboring molecules, and there are no connections of the type "atomic sphere – empty sphere – atomic sphere." Due to large distance, the overlap of electronic orbitals between different molecules is negligible, and our calculations show that the location and radii of the empty spheres do not play an important role.

Another issue is the number of k-points used for integration over the irreducible part of the Brillouin zone. In our calculations, we use the following procedure. As a first step, we perform a self-consistent calculation for one k-point, which gives us a good starting point for further calculation with larger number of k-points and ensures good stability of numerical calculation. As a second step, we make a calculation with minimal division of the Brillouin zone, i.e., with two k-points in every direction; for V_{15}, this gives us eight k-points in total, and six k-points in the irreducible part of the Brillouin zone. After that, we make calculations with larger number of k-points. However, we consistently find that the significant increase in the number of k-points (up to 65 points in the irreducible part of the Brillouin zone) does not noticeably change the results (magnetic moments stay the same and exchange interactions vary by no more that ~2 %). Similar results have been also obtained for other magnetic molecules, e.g., for Mn_{12}, variation in the number of k-points from 4 to 134 per irreducible part of the Brillouin zone, changes the exchange interactions only by ~7 %.

From a body of previous works, it is known that LDA+U ASA-LMTO method gives good results for vanadium-oxide systems (see e.g., Refs. 13,20). The calculations presented below have been performed for the values of the on-site repulsion parameter U varying from 4 to 5.2 eV with the constant Hund's exchange parameter $J=0.8$ eV. These are typical values for vanadium-oxide crystal systems; the first-principle estimates[13,20] for U give the values ranging from 3.6 eV to 6.7 eV, depending on the oxidation degree and the crystal structure. In our previous work,[21] we have found that the values of U near 4 eV provide a good agreement of the calculated band structure with the results of x-ray photoelectron and x-ray emission spectroscopy.

Below, we present the results for three types of magnetic ordering in the V_{15} molecule. The antiferromagnetic structure denoted below as AFM1 corresponds to the situation when the magnetic moments of the V1 and V3 ions are directed down and the moments of the V2 ions are directed up. The antiferromagnetic structure AFM2 corresponds to the V2 and V3 moments directed up and the V1 moment directed down. The ferromagnetic structure FM corresponds to all moments directed down. The AFM1 and AFM2 structures correspond to low-energy spin states of the V_{15} molecule, while FM corresponds to a highly excited spin state. It is important to note that the true ground state of V_{15} is a complex superposition of different states of the system of 15 quantum-mechanical spins $1/2$, and the direction of a given spin $1/2$ cannot be defined even approximately. As a result, incorporation of the results of the electronic band structure calculations into a quantum spin Hamiltonian is a very complex issue. One possible solution, adopted in Refs. 11,12 is to calculate the *total energies* of different spin configurations and to fit them with the mean-field results for a Heisenberg spin Hamiltonian. Here, we use a different strategy: we calculate the *exchange parameters* using the Green's function method, as a second derivative of the energy variation at small rotations of the quantization axes of spins $1/2$. The details of this method are described in Refs. 22 and 23, and its previous application to Mn_{12} magnetic molecules is described in Ref. 18. It appears that the exchange parameters calculated for different spin configurations in V_{15} molecule are very close to each other, i.e., Heisenberg spin Hamiltonian is a good approximation for V_{15}, and the calculated exchanges can be plugged in the spin Hamiltonian directly. The effective spin Hamiltonian has been diagonalized, and the resulting eigenenergies and eigenfunctions have been used to calculate the experimentally relevant quantities (magnetic susceptibility, magnetic moment of the molecule, distances between different energy levels, etc.).

Finally, we mention that the graphs for the electronic density of states (DOS) presented below were smeared, following the standard practice, by convolution of the calculated energy levels with the Gaussian line of the width 0.1 eV.

II. RESULTS OF CALCULATIONS

Figure 2 presents densities of states for *d* electrons of nonequivalent vanadium ions V1, V2, and V3; these DOS have been calculated for $U=4$ eV and $J=0.8$ eV; the spin configuration is AFM1 (spins of V1 and of V3 are down, spins of V2 are up). Previous magnetic measurements[6–8] confirm that all V ions are tetravalent, with the well-defined total spin $1/2$ per ion. Moreover, the dc-spin susceptibility and EPR 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 3*d* 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 eV and -7 eV. The sharp peaks correspond to localized V *d*-electrons responsible for formation of well-defined local spins $S=1/2$ of vanadium ions. Our calculations, indeed, result in 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 broadbands in the spectrum of V *d* electrons clearly demonstrate the signatures of hybridization between the V *d* and the O *p* states. The broad structure of O *p* 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 (~800 K, according to Ref. 7), and involve strong hybridization between V 3*d* and oxygen 2*p* orbitals. Much weaker interactions of V3 ions are due to weaker *p*-*d* hybridization and larger V3-V3 distances.

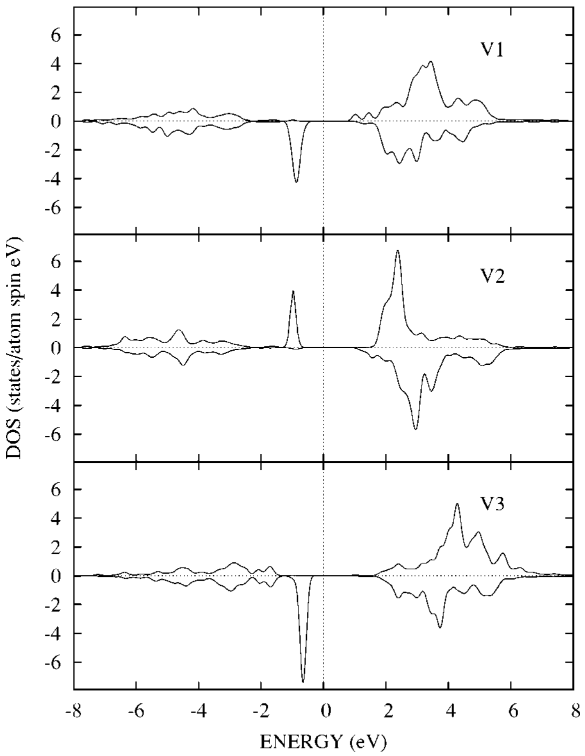

FIG. 2. DOS of *d*-electrons of inequivalent V1, V2, and V3 ions. The DOS are calculated for $U=4$ eV and $J=0.8$ eV; the spin configuration is AFM1 (spins of V1 and of V3 are down, spins of V2 are up).

For larger values of the on-site repulsion parameter *U*, the DOS do not significantly change, but the distance between the bands increases with *U*. This is demonstrated in Fig. 3, where the vanadium *d* and oxygen *p* DOS are presented for different values of *U*. With increasing *U*, the unoccupied vanadium bands move farther from the Fermi level (taken as zero energy), and the oxygen bands move closer to the Fermi level due to hybridization with the occupied vanadium bands. The peaks in the V *d* bands which correspond to the electrons localized on the vanadium ions, remain well pronounced for $U=4$ and 5 eV. For larger *U*, the bands overlap thus leading to a strong hybridization and to noticeable changes in the band structure. The sharp peaks in the V *d* band become broadened, and the magnetic properties of V_{15} change (e.g., the calculated exchange interaction parameters

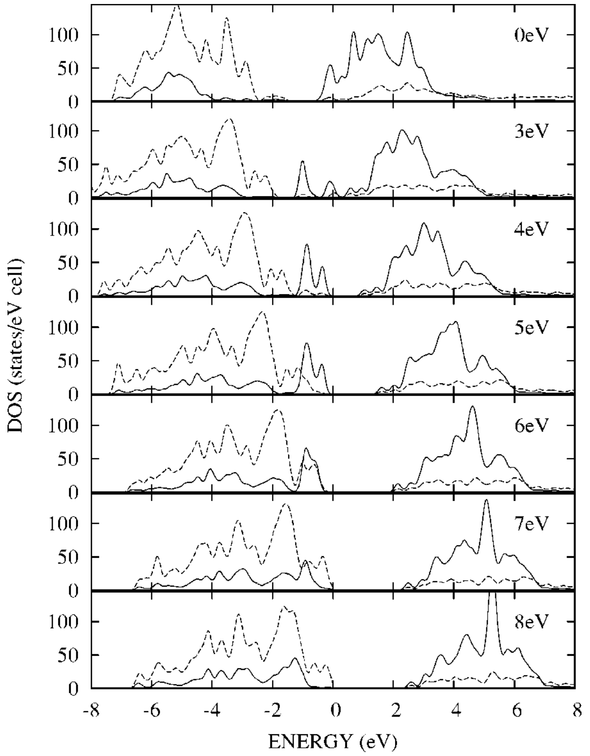

FIG. 3. Dependence of the $2p$ oxygen (dashed lines) and $3d$ vanadium (solid lines) DOS on the Coulomb repulsion parameter U, for the values of U from 0 eV to 8 eV.

decrease by a factor of three), but magnetic moments of all vanadium atoms do not change appreciably staying close to 1.0 μ_B.

To make 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. The value of the electronic gap can be estimated from the results of optical measurement. The data presented in Ref. 24 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 the optical measurements, but other values of the gap can also be compatible with the experiment. To make a rigorous comparison, more extensive calculations are needed that take into account the values of matrix elements between different electron states. Corresponding work is in progress now.

The sharp peaks in V $3d$ DOS responsible for the formation of the well-defined spin $1/2$ of the vanadium ions are very robust with respect to small changes both in U and in magnetic structure of the molecule. As a result, the spin states of the vanadium ions are almost independent on magnetic structure of the molecule. This point is illustrated by Table II, where we present the results for different spin orientations of the vanadium spins, using $U=4$ eV and $J=0.8$ eV. The calculations have been made for the three configurations mentioned above: AFM1 (the spins of V1 and V3 are down, the spins of V2 are up), AFM2 (the spins of V1 are down, the spins of V2 and V3 are up), and FM (all spins down). The AFM1 and AFM2 structures corresponds to the low-energy spin states of the V_{15} molecule, while FM corresponds to a highly excited spin state (see the value of the exchange parameter J in Table I). As one can see, for all three structures, the differences in magnetic moments, electronic gap, and the exchange interaction parameters are rather small. Moreover, if we compare differences in the values of the exchange parameters for different values of U and for different spin configurations, we can see that the changes of the spin configurations and the variation of the parameter U by ~ 0.5 eV result in corresponding small changes of the exchange parameters, thus giving an indirect estimate of the accuracy of the calculated exchange parameters. Therefore, we have a good evidence that the Heisenberg isotropic exchange is a valid approximation for the exchange interactions between vanadium ions in V_{15}.

Thus, we can confidently apply the spin Hamiltonian approach to study the spin states of the V_{15} molecule. In this paper, we consider only the isotropic part of the spin Hamiltonian in the Heisenberg form

TABLE I. The values of exchange parameters (in Kelvin), gap in the electronic spectrum, and the distance ΔE between the spin ground state and the first excited spin state for different values of U: $U=4.2$ eV, 4.8 eV, 5.0 eV, 5.2 eV, and 5.4 eV. All the values are calculated for the spin structure AFM1.

atom 1	atom 2		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
	ΔE, K		8.38	6.51	4.92	4.85	4.79

TABLE II. The exchange parameters (in Kelvin), electronic gap, and the magnetic moments of V ions for different magnetic structures of V_{15}. The calculations have been made for $U=4$ eV, $J=0.8$ eV.

parameter	AFM1	AFM2	FM
J	−910	−905	−942
J'	−45	−46	−53
J''	−136	−139	−156
J_1	−219	−247	−255
J_2	−134	−128	−132
J_3	−5	−5	−6
J_4	−13	−12	−15
J_5	−3	−3	−3
J_6	−3	−3	−3
gap	1.08	1.02	1.16
μ_{V1}	−0.94	−0.93	−0.99
μ_{V2}	+0.91	+0.92	−0.97
μ_{V3}	−1.00	+0.97	−1.00

$$\mathcal{H}=-\sum_{m<n} J_{mn}\mathbf{S}_m\mathbf{S}_n, \tag{1}$$

where $\mathbf{S}_m$ and $\mathbf{S}_n$ are the exchange coupled vanadium spins $1/2$, and J_{mn} is the corresponding coupling parameter; note the summation over pairs of spins. Using the calculated values of the exchange parameters, we have performed exact diagonalization of the spin Hamiltonian of V_{15}. As a result, we obtain the energy difference ΔE between the spin ground state and the first excited spin state. In all the cases studied, the total spin of the ground state is $S_{tot}=1/2$, and the total spin of the first excited state is $S_{tot}=3/2$. The experimental value $\Delta E_{\exp}=3.7$ K is known from magnetic measurements,[9] and from the neutron scattering experiments.[25] As one can see from the Table I, the calculated values of ΔE 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 exchanges (20–30 % is a typical precision of such calculations), or by omission of anisotropic interactions, which are noticeable at this energy scale.[9,10,25] Also, using the exact diagonalization results, we have calculated the temperature dependence of the effective magnetic moment of the molecule $\mu(T)=\sqrt{3\chi(T)\cdot k_B T}$, where $\chi(T)$ is the temperature-dependent magnetic susceptibility of a V_{15} molecule [$\chi(T)$ is the experimentally measured quantity], and k_B is Boltzmann's constant. The results of these calculations are presented in Fig. 4, along with the experimental data measured by one of us on a freshly grown sample of V_{15} in the field of 0.5 Tesla. One can see that all theoretical curves are very close to the experimental data, i.e., the values of U in the region close to 4–5 eV result in good agreement with the experimental data.

It is interesting to compare the set of exchange parameters for V_{15} molecule obtained by LSDA (Ref. 11) and LDA+U methods. On top of a simple rescaling factor of about 2 for all exchange parameters, there are large differences for the two largest exchanges: J differs by a larger factor, about 3.7, and J' has different sign. We believe that this "nonuniform" scaling is the result of different electronic structure, or much smaller V-O covalency effects in the LDA+U calculations, in comparison with the LSDA results.

This difference in the exchange interaction parameters leads to a qualitative difference in the spectra of the Heisen-

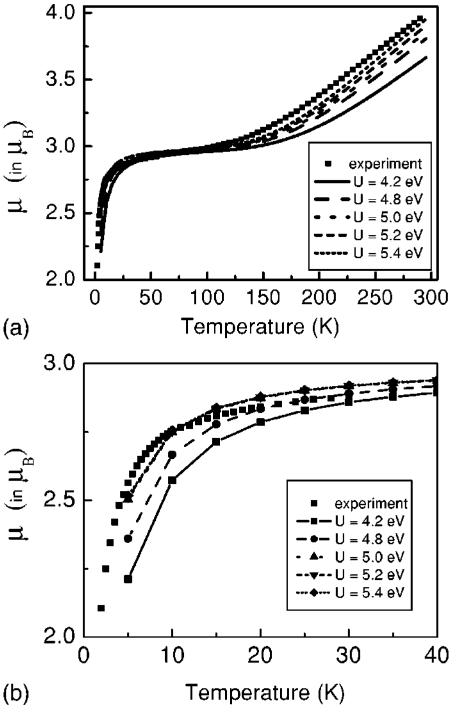

FIG. 4. (a) Temperature dependence of the effective magnetic moment of V_{15} molecule. Theoretical curves are calculated using the exchanges corresponding to different values of U. Experimental results, obtained in the field of 0.5 Tesla, are presented for comparison. All calculated curves corresponding to U near 5.0 eV are close to the experimental curve. (b) The low-temperature part of these data presented in more detail.

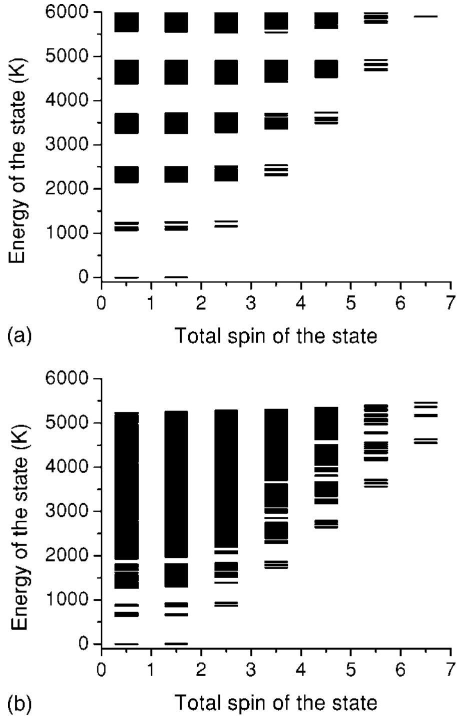

FIG. 5. The spin-Hamiltonian spectra of V_{15}. The spectra were obtained by diagonalizing the Heisenberg-exchange spin Hamiltonian with the exchange parameters derived from: (a) LSDA (the exchange parameters were taken from Ref. 11 and divided by 2.9, as suggested there); (b) from LSDA+U calculations with $U=5$ eV, without any extra scaling. The upper graph (a) shows only the low-energy part of the spectrum because the highest levels in this case have energies above 7000 K.

berg spin Hamiltonians. In Fig. 5, we present the spectra of spin Hamiltonians calculated by using the exchange parameters from LSDA (taken from Ref. 11) and LDA+U calculations. The LSDA exchange parameters were divided by a factor of 2.9, as suggested in Ref. 11, which is needed to achieve agreement with experimental data. The LDA+U exchange parameters used in Fig. 5 were calculated for $U=5$ eV, but all other values of U give very similar picture. Both LSDA and LDA+U sets of exchange parameters give two degenerate $S_{tot}=1/2$ (doublet) states as ground states, and one $S_{tot}=3/2$ (quadruplet) state as a first excited state with energy $\Delta E \sim 4\text{-}5$ K. However, the high-energy part of the spectra are qualitatively different. The LDA+U exchange parameters give an almost continuous spectrum, which starts at about 600 K, with the highest energy level at about 5500 K. The LSDA exchanges result in a spectrum with well-defined bands of excitations, which starts at more than 1000 K, with the highest energy level at about 7200 K. The "banded" spectrum resulting from the LSDA exchange parameters leads to noticeable discrepancies between theoretical and experimental $\mu(T)$ curves at temperatures higher than 150 K (see Fig. 2 in Ref. 11). Such discrepancy is absent for the LDA+U exchange parameters.

III. SUMMARY

Summarizing, we have performed theoretical investigation of electronic structure of V_{15} magnetic molecules using LSDA+U electronic structure calculations. We show that the account of the on-site Coulomb repulsion allows one to achieve quantitative agreement with known experimental facts. The calculated magnetic moments of individual vanadium ions correspond to the well-localized spins 1/2 on vanadium sites. For the values $U \sim 4\text{-}5$ eV of the on-site Coulomb repulsion parameter, good description of V_{15} electronic and magnetic properties has been obtained. The values of electronic gap are compatible with the results of optical measurements. Using the exchange couplings calculated for $U \sim 4\text{-}5$ 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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