Electronic Structure of Vanadium Cluster Anions
− Measurement and DV-$X\alpha$ Calculation of Photoelectron Spectra −

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Photoelectron spectra of vanadium cluster anions, V_n^- ($3 \leq n \leq 100$), were measured at the photon energy of 3.49 eV by using a magnetic-bottle-type photoelectron spectrometer. A spin-polarized DV-$X\alpha$ method was adopted to calculate electronic structures of V_4^- with several possible geometric structures. These calculated spectra were compared with that obtained by the experiment to examine a geometric structure and magnetic properties of V_4^-. It is revealed that V_4^- is spin-polarized and has ferromagnetic spin coupling. Size-dependent change in electronic affinities of V_n^- is explained in terms of a spherical conducting droplet model.

KEYWORDS: vanadium cluster anions, photoelectron spectrum, DV-$X\alpha$ method, electronic structure

1. Introduction

A vanadium metal in bulk is known to be nonferromagnetic at all temperatures, while a two dimensioned vanadium layer exhibits ferromagnetic behavior[1] It seems that the coupling scheme is critically dependent on the interatomic distance in the vanadium system. Therefore, a vanadium cluster provides an unique opportunity to investigate the size-dependent magnetic coupling scheme. Magnetism of small vanadium clusters is studied by various calculations and experiments[1-13]. A calculation shows that atomic V_{15} having a bcc structure with the bulk interatomic spacing is nonmagnetic[2-5], whereas V_9 having a bcc structure with the bulk interatomic spacing possesses a magnetic moment per atom of $2.89\mu_B$, as studied by the discrete variational method[2]. Lee and Callaway have calculated typical magnetic low- and high-spin moments per atom to be 0.33 and $2.78\mu_B$, on the assumption of a bcc structure with the bulk internuclear spacing[3]. The Stern-Gerlach experiment by Douglass et al. has revealed that the maximum moment per atom of V_9 is $0.59\mu_B$ when superparamagnetism is assumed[6]. These studies have predicted that small vanadium clusters are ferromagenetic. However, their magnetic properties are remained to be studied because the geometric structures of those clusters cannot simply be determined. It is indicated that a vanadium metal becomes ferromagnetic when its lattice parameter is increased or its size and dimension are constrained[2]. Evidently, it is important to decide the geometric structure for the investigation of the magnetic properties of small vanadium clusters.

In a vanadium cluster, the valence d-electrons tend to be localized, particularly in the clusters with a small sizes. It is, therefore, expected that a size-dependent change in the electronic structure of the vanadium cluster occures at a certain cluster size. In fact, in the previous study on cobalt clusters, a size-dependent transition in the electronic structure is found to occur at $n \approx 7$ by comparing measured electron affinities of metal clusters with those predicted by a spherical conducting droplet model[14].

To this end, photoelectron spectra of vanadium cluster anions, V_n^- ($3 \leq n \leq 100$), were measured using a laser-vaporization cluster source and a magnetic bottle type photoelectron spectrometer. Those spectra were compared with the results of the spin-polarized DV-$X\alpha$ calculation for V_4^-. Size-dependent change in electronic properties of these clusters is analyzed by a spherical conducting droplet model.

2. Experiment

The experimental setup is almost the same that used in the cobalt cluster studies, and has been described elsewhere[14]. A schematic drawing of the apparatus is shown in Fig.1. Vanadium cluster anions, V_n^-, were produced by laser vaporization in a small cluster-growth chamber[15, 16]. A disk made of vanadium matal was rotated and translated, on which the second harmonics of a Q-switched Nd:YAG laser (Spectra Physics DCR-11) was focused. A helium carrier gas was introduced by a pulsed valve (General Valve series 9) into the cluster-growth chamber and was mixed with vanadium metal vapor. Cluster ions generated and cooled in this small
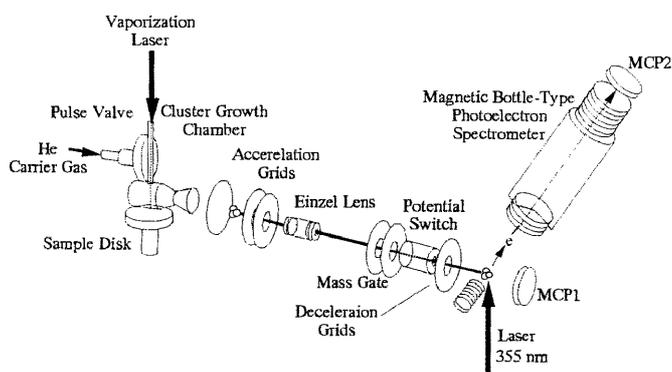

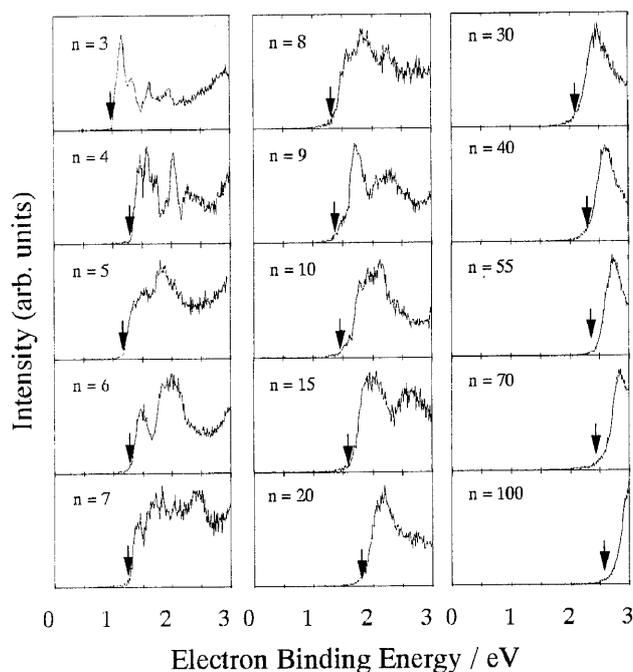Fig.1. Schematic diagram of the experimental apparatus.

Fig.2. Photoelectron spectra of vanadium cluster anions, V_n^-, measured at 355 nm laser (3.49eV). The onset energies providing the electron affinities (EA) are indicated by the arrows in the spectra.

chamber were admitted into vacuum through a hypersonic conical nozzle, then were accelerated to 500-1,000 eV by applying pulsed voltage to double acceleration grids of a Wiley-McLaren-type time-of-flight mass spectrometer[17]. Cluster beam was focused by adjusting the voltage applied to the acceleration grids and an einzel lens. The ions were detected by a microchannel plate (Hamamatsu F2223-21S), MCP1. The signals from the detector were amplfied and stored in a trangient digitizer (Iwatsu DM-2350) with a time resolution of 20 ns. Typically 500 events were accumulated to obtain the mass spectra of V_n^-.

The cluster anions were mass-selected by using a three-grid mass gate, and were deccelerated to the kinetic energy of 30-100 eV by a potential switch and decceleration grids before it was allowe to enter into a photoelectron spectrometer[18, 19]. Size-selected cluster anions were irradiated by the third harmonics of a Nd:YAG laser (Spectra Physics GCR-250-10), having a fluence of 10-25 mJ cm^{-2}. The kinetic energy of photoelectrons thus produced was measured by a magnetic-bottle-type time-of-flight spectrometer, with a magnetic field of $\sim$ 400 G in the detatchment region followed by a weak homogeneous magnetic field of $\sim$10 G. The signals of the photo electrons, from a microchannel plate (Hamamatsu F2223-21S), were amplified, discriminated, and digitized with a 4-ns time resolusion. The data were accumulated for 20,000-50,000 events. The time-of-flight of the photoelectrons was converted to the kinetic energy after calibrating the system by measuring a photoelectron spectrum of Cu$^-$ measured simultaneously. All the spectra were smoothed over a 0.005-eV square window. The overall energy resolution was better than $\Delta E/E = 0.01$. The vacuum chamber for the photoelectron spectrome-
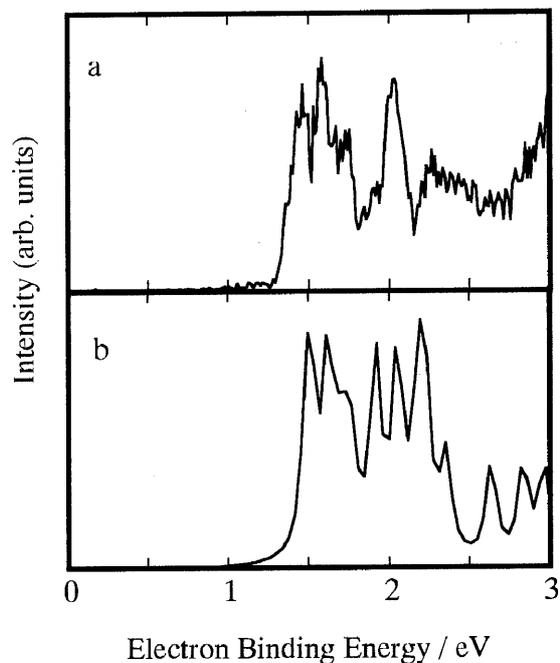

Fig. 3. Photoelectron spectra of V_4^-. (a) Experimental spectrum and, (b) that calculated by the spin-polarized DV-$X\alpha$ method for D_{4h} symmetry with the bond-distance of 5.82 a.u..

ter was maintained at a pressure less than 2×10^{-9} Torr. The background signal associated with residual gas was less than 10 % of the total photoelectron signals.

3. Results

Typical photoelectron spectra for V_n^- ($3 \leq n \leq 100$) are shown in Fig.2. at the photon energy of 3.49 eV (355 nm). The uncertainties in the relative photoelectron intensities were estimated to be less than 10 % from the reproducibility of different experimental runs. The photoelectron spectrum of V_3^- has four intense peaks in 1-2 eV, while that of V_4^- has more complicated structures in the same energy range. As the cluster size, n, increases, the spectrum tends to be structure-less. It is evident that the onset energy of the spectrum increases gradually with n.

4. Discussion

4.1. Geometric and Electronic Structures

Calculations by the spin-polarized DV-$X\alpha$ method were performed to obtain information about electronic and geometric structures and magnetic properties of V_4^-. The exchange parameter was fixed to be 0.70, and atomic orbitals of $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, and $4p$ were used as the basis set, which were calculated numerically by the Hatree-Fock-Slater method. For $4p$ orbitals, a well potential of 0.1 a.u. were added throughout the calculations. Calculations were repeated until the difference of the number of the electrons projected on each atomic orbital becomes less than 0.0002 (self-consistent charge method). All the calculations were carried out by using a workstation (SUN, SPARK station IPX).
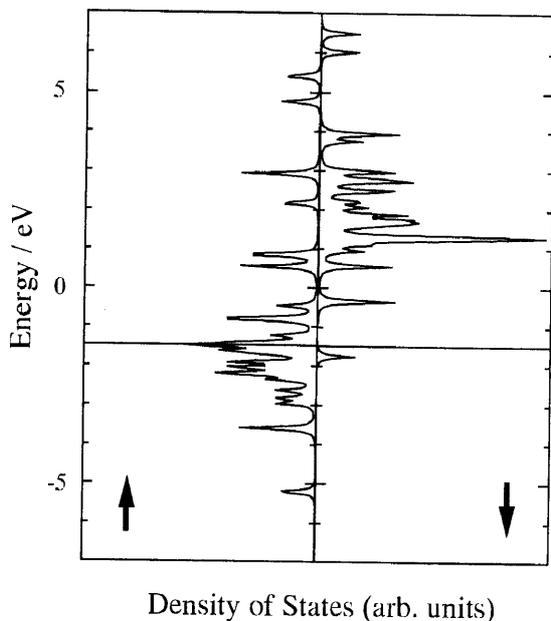
Density of States (arb. units)

Fig.4. Density-of-states profiles of V_4^- with the majority (up) and minority (down) electron spins. Fermi energy is indicated by the horizontal line.

In order to calculate the transition energies the transition-state method was adopted. Energy levels for the transition state, which has the HOMO electron less by 0.5 than the corresponding anion, were calculated to obtain the difference of electronic structures between an anionic and a neutral cluster. Each transition energy was broadened by a Lorentzian function and were summed up to obtain the photoelectron spectrum for the comparizon with the photoelectron spectrum of V_4^- measured.

The molecular orbitals obtained were used to further calculate electron and spin distributions were calculated by Mulliken population analysis.

The result of a tetramer anions is described in the following. Most probable structures of tetrahedral(T_d) and equilateral square(D_{4h}) were tried for the spectrum calculations for V_4^-. The interatomic distance used here were 3.74 a.u.(dimerdistance), 5.54 a.u.(nearest neighbor distance in the bulk), 4.99 a.u.(90 % of the bulk value), 5.82 a.u.(105 % of the bulk value), and 6.09 a.u.(110 % of the bulk value). The spectra calculated for each geometry was compared with the experimental one.

The observed spectrum was well reproduced by the spectrum calculated on the sturcture with a D_{4h} symmetry with a bond length of 5.82 a.u., which is 5 % longer than that of bulk. The calculated and measured spectra are shown in Fig.3. The electron affinity is calculated to be 1.48 eV, which agrees well with the experimental value of 1.32 eV within the error inherent to the DV-$X\alpha$ calculation.

4.2. Magnetic Moment and Exchange Energy

Density of states(DOS) of V_4^- was obatained by broadening the energy levels by using a Lorentzian function, which is shown in Fig.4. The DOS curve shows that the $3d$ band possessing the majority spin is almost filled, while that possessing the minority spin is unoccupied
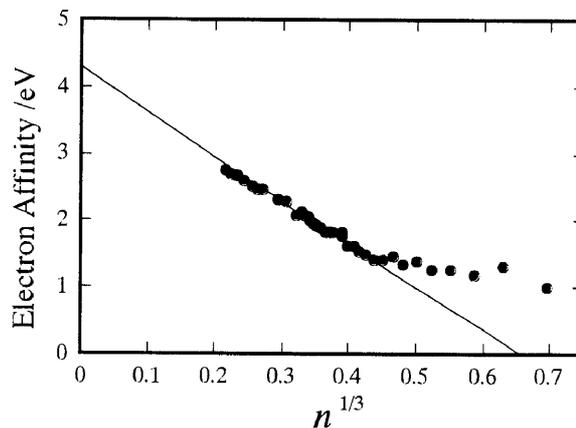

Fig.5. Electron affinities as a function of the value of $n^{1/3}$. The solid line represents the prediction by the spherical conducting droplet model [see Eq. (1) in the text].

and extends above a Fermi level. The difference in number density between the majority and the minority spin (spin difference) was determined. The average spin-difference per vanadium atom for V_4^- turned out to be 1.2. The average energy difference between the majority and the minority spin states is calculated to be 1.85 eV, which is closely connected to the exchange energy. The spin difference and the exchange energy indicate that V_4^- has a ferromagnetic spin coupling.

4.3. Evolution of Electronic Structure

If a cluster is assumed to be a spherical metallic conductor with a radius R, its electron affinity (EA) can be expressed as,

$$EA = W - \alpha \frac{e^2}{R} \quad \text{22-24)}, \tag{1}$$

where W represents the work function of the bulk conductor and e is the electron charge[20]. The cluster radius is written as,

$$R = dn^{1/3} + r_0, \tag{2}$$

where d is the nearest neighbor distance and r_0 is a parameter to account for "spilling out" of the electron charge beyond the boundary of the cluster[21]. The solid line in Fig.5 represents the $EA - n^{-1/3}$ curve calculated from Eqs.(1) and (2) with $W = 4.30$ eV, $\alpha = 5/8$, $d = 1.31$ Å, where the nearest neighbor distance of vanadium metal, and r_0 of 0.1 Åare employed. As shown in Fig.5, the calculation reproduces the experimental data in the $n \geq 9$ range. The deviation of the experimental data from the calculation below $n = 9$ shows that the electronic properties change at $n = 9$; a similar size-dependent transition in the electronic properties.

5. Conclusion

The photoelectron spectra of $V_n^-(3 \leq n \leq 100)$ were measured at the photon energy of 3.49 eV. For $n = 4$, the electronic structures were calculated by the spin-polarized DV-$X\alpha$ method and the energy levels were obtained by comparing the calculated spectra with the

observed one. The valence electrons are found to be spin-polarized.

The electron affinities were determined as a function of the cluser size, n. In the range of $n \geq 9$, the electron affinity follows the value predicted by the spherical conducting drop model, while the electron affinity deviates from the prediction in the range of $n < 9$. The deviation indicates that there is a size-dependent change in electronic property at $n \approx 9$.

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1) C. L. Fu, a. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985)

2) F. Liu, S. N. Khanna, and P. Jenna, Phys. Rev. B **43**, 8179 (1991)

3) K. Lee and J. Callaway, Phys. Rev. B **49**, 13906 (1994)

4) P. Alvarado, J. Dorántes-Davila, and H. Dreyssé, Phys. Rev. B **50**, 1039 (1994)

5) D. R. Salahub and R. P. Messmer, Sur. Sci. **106**, 415 (1981)

6) D. C. Douglass, J. P. Bucher, and L. A. Bloomfield, Phys. Rev. B **45**, 6341 (1992)

7) V. L. Moruzzi, Phys. Rev. Lett. **57**, 2211 (1986)

8) V. L. Moruzzi, P. M. Marcus, and P. C. Pattnaik, Phys. Rev. B **37**, 8003 (1988)

9) J. Dorantes-Dávila and H. Dreyssé Phys. Rev. B **47**, 3857 (1993)

10) H. Akoh and A. Tasaki, J. Phys. Soc. Jpn. **42**, 791 (1977)

11) C. Rau, C. Liu, A. Schmalzbauer, and G. Xing, Phys. Rev. Lett. **57**, 2311 (1986)

12) C. Rau, G. Xing, C. Liu, and M. Robert, Phys. Lett. A **135**, 227 (1989)

13) R. L. Fink, C. A. Ballentine, J. L. Erskine, and J. A. Araya-Pochet, Phys. Rev. B **41**, 10175 (1990)

14) H. Yoshida, A. Terasaki, K. Kobayashi, M. Tsukada, and T. Kondow, J. Chem. Phys. **102**, 5960 (1995)

15) P. Milani and W. A. de Heer, Rev. Sci. Instrum. **61**, 1835 (1990)

16) J. P. Bucher, D. C. Douglass, and L. A. Bloomfield, Rev. Sci. Instrum. **63**, 5667 (1992)

17) W. C. Wiley and I. H. McLaren, Rev. Sci. Instrum. **26**, 1150 (1955)

18) P. Kruit and F. H. Read, J. Phys. E **16**, 313 (1983)

19) O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, and R. E. Smalley, Rev. Sci. Instrum. **58**, 2131 (1987)

20) D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. **99**, 8542 (1993)

21) D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. **86**, 1715 (1987)

22) D. M. Wood, Phys. Rev. Lett. **46**, 749 (1981)

23) M. Seidel, K. -H. Meiwes-Broer, and M. Brack, J. Chem. Phys. **95**, 1295 (1991)

24) W. A. de Heer, Rev. Mod. Phys. **65**, 612 (1993)