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Ab Initio Study on the Electronic, Magnetic, and Mechanical Properties of $CaCu_3V_4O_{12}$

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The electronic, magnetic, and mechanical properties of $CaCu_3V_4O_{12}$ are investigated by use of the density functional theory method. The calculated results indicate that $CaCu_3V_4O_{12}$ is a half-metallic and ferrimagnetic compound. The magnetic coupling for Cu−V is antiferromagnetic, while those for Cu−Cu and V−V are ferromagnetic. The obtained elastic constants suggest that the compound is mechanically stable. The calculated oxidation states and density of states reveal the existence of a mixed valence for Cu and V. This supports the experimental observation of the mixed valence in $Ca^{2+}Cu^{2+}Cu_2{}^{+}(V_2{}^{5+}V_2{}^{4+})O_{12}$.

Introduction

The complex compounds $CaCu_3B_4O_{12}$ (B = transition metal) are rich in both physics and chemistry. From the experimental point of view, $CaCu_3Mn_4O_{12}$ was reported to be a ferrimagnetic semiconductor with a quite large magnetoresistance at relatively low magnetic field over a wide temperature range.[1] $CaCu_3Ti_4O_{12}$ has the largest dielectric constant (10^5) over a wide temperature range ever measured.[2–5] $CaCu_3Cr_4O_{12}$ was a Pauli paramagnetic metal.[6] For $CaCu_3Ru_4O_{12}$, early experimental studies showed that it is a Pauli paramagnetic metal,[7,8] while further experimental studies found that it is a new d-electron heavy-fermion system, and its electronic structure best resembles that of the f-electron Kondo system.[9,10] $CaCu_3V_4O_{12}$ has been recently synthesized by Volkov et al.[11] It shows metallic conductivity from room temperature to 300 °C and antiferromagnetic ordering below 90 K with an effective magnetic moment $\mu_{\mathrm{eff}} \sim 0.7\ \mu_{\mathrm{B}}$.[11] X-ray photoelectron spectroscopy (XPS) revealed that Cu and V are in a mixed-valence state, and the compound is formulated as $Ca^{2+}Cu^{2+}Cu_2{}^{+}(V_2{}^{5+}V_2{}^{4+})O_{12}$.[11] Interestingly, from experiment,[11] the mixed-valence atom Cu ($Cu^{2+}Cu_2{}^{+}$) has the same chemical environment and the same oxidation state, and it is also true for V ($V_2{}^{4+}V_2{}^{5+}$). From the previous work of Robin and Day,[12] it is known that the mixed-valence compounds can be classified into three different classes. For class I mixed-valence compounds, the coordination environments are quite different for the ions of each oxidation state. For class II mixed-valence compounds, although the coordination environments are still different for the ions of each oxidation state, the sites are sufficiently similar so that electron transfer can occur with only a small input of energy, while for the class III mixed-valence compounds, the mixed-valence atoms have the same chemical environment and the same oxidation state. Thus, $Ca^{2+}Cu^{2+}Cu_2{}^{+}(V_2{}^{5+}V_2{}^{4+})O_{12}$ could be regarded as the class III mixed-valence compound. Of particular interest is

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that, upon cooling, charge ordering may occur by transformation of the class III mixed-valence compounds to class I mixed-valence compounds.[12]

On the theoretical side, extensive studies were available. For $CaCu_3Mn_4O_{12}$, although a theoretical study by local spin density approximation (LSDA) showed that it is a ferrimagnetic metal,[13,14] LSDA+U[13] (U indicates on-site Coulomb interaction) and generalized gradient approximation[15,16] (GGA) calculations indicated that it is a semiconducting ferrimagnet, confirming the experimental observation.[1] A theoretical study on $CaCu_3Ti_4O_{12}$ by LSDA and GGA indicates that it is an antiferromagnetic insulator,[14,17–19] in agreement with experiment.[2,3,20,21] For $CaCu_3Cr_4O_{12}$, LSDA study gave a ferrimagnetic configuration,[14] while the GGA calculation yields both a ferrimagnetic and a half-metallic solution.[22] A theoretical study by LSDA[14,23] and GGA[24] on $CaCu_3Ru_4O_{12}$ confirms the experimental observation[7,8] that it is a paramagnetic metal. $CaCu_3Fe_4O_{12}$ has been recently predicted to be a ferrimagnetic and half-metallic compound by the GGA+U method.[25] In this paper, to gain further understanding on $CaCu_3V_4O_{12}$, we have studied the electronic, magnetic, and mechanical properties of the compound by use of density functional theory.

Computational Methods

The geometry optimization was performed by use of the CASTEP code.[26] The Vanderbilt ultrasoft pseudopotential[27] was used with a cutoff energy of 340 eV. The exchange and correlation functionals were treated by GGA in the formulation of Perdew, Burke, and Ernzerhof (GGA-PBE).[28] The elastic constants of $CaCu_3V_4O_{12}$ were also evaluated within the CASTEP code. The studies of electronic and magnetic properties were performed using the *WIEN2K* program.[29,30] It is based on the full-potential linearized augmented plane-wave (FPLAPW) method with a dual basis set. In FPLAPW calculations, GGA-PBE was used as the exchange correlation potential.[28] The muffin-tin radii (R_{MT}) are considered to be 2.42, 1.97, 1.92, and 1.70 bohr for Ca, Cu, V, and O, respectively. The plane-wave expansion cutoffs are 7.0 for expanding the wave function (RKMAX) and 14 for expanding the densities and potentials (GMAX). In the complete Brillouin zone 1000K points were used. The Brillouin zone integration is carried out with a modified tetrahedron method.[31] The self-consistent-field calculations were considered to be converged when the energy convergence is less than 10^{-5} Ry. In addition, the electron–electron Coulomb interactions for Cu and V are considered in a rotationally invariant way (GGA+U).[32] In this paper, the effective parameter $U_{eff} = U - J$ was adopted, where U and J are the Coulomb and exchange parameters, respectively. For simplicity, we use U to denote the effective parameter in the following paper, instead of U_{eff}.

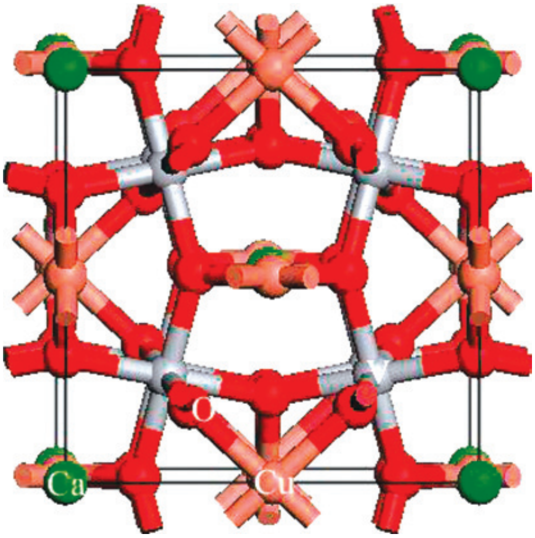

Figure 1. Crystal structure of $CaCu_3V_4O_{12}$.

Results and Discussion

Although $CaCu_3V_4O_{12}$ was reported to crystallize in the $Im\bar{3}$ phase,[11] the fractional coordinates were not available. Therefore, we choose the isostructural $CaCu_3Cr_4O_{12}$[6] as the initial structure by substituting V for Cr. The geometry optimization was performed on $CaCu_3V_4O_{12}$ under both nonspin polarization (NSP) and spin polarization (SP) cases. The results indicate that SP is lower in energy than NSP by 31.2 meV per formula unit. Therefore, in the following, we will only show the results from the SP case. The crystal structure is shown in Figure 1. The obtained unit cell parameter from SP (a = 7.3210 Å) is close to the experimental value (a = 7.28453 Å).[11] The calculated fractional coordinates are (0, 0, 0) for Ca, (0.5, 0, 0) for Cu, (0.25, 0.25, 0.25) for V, and (0.3005, 0.1830, 0) for O. The coordination numbers are 12, 6, and 4 for Ca, V, and Cu, respectively. In VO_6 octahedra, the O−V−O angles are 89.4° and 90.6°, respectively, instead of 90° in an ideal octahedron. Thus, the VO_6 octahedra are distorted from the ideal O_h symmetry to S_6 symmetry. On the other hand, for CuO_4, the

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Table 1. Calculated Total Net Magnetic Moment M_{tot} per Formula Unit (in Bohr Magneton, μ_B), Magnetic Moment (in μ_B) of Cu (M_{Cu}), V (M_V), and O (M_O) Ions, and the Energy Band Gap E_g (in eV, at the Spin-Down Channel) in $CaCu_3V_4O_{12}$ from GGA and GGA+U (in Ry) Calculations (Different U_{Cu} and U_V Values Are Selected)

U_{Cu}	0.00	0.30	0.30	0.40	0.40	0.50	0.60
U_V	0.00	0.00	0.10	0.20	0.30	0.30	0.40
M_{tot}	0.98	1.00	1.00	1.00	1.00	1.00	1.00
M_{Cu}	−0.23	−0.49	−0.51	−0.59	−0.61	−0.66	−0.73
M_V	0.49	0.72	0.79	0.89	0.94	0.95	1.01
M_O	−0.05	−0.07	−0.09	−0.11	−0.12	−0.11	−0.12
E_g	0.00	1.30	1.46	1.68	1.85	2.12	2.58

O−Cu−O angles are 94.9° and 85.1°, respectively, indicating that the symmetry of CuO_4 is lowered from an ideal planar square with D_{4h} symmetry to a planar rectangular shape with pseudo-D_{4h} symmetry. The considerable size mismatch and difference in the bonding requirements for Ca and Cu lead to the deviation of the V−O−V angle (142.9°) from the ideal 180° by the tilting of VO_6. The calculated bond lengths of Cu−O and V−O are 1.982 and 1.926 Å, respectively. According to the bond valence sums (BVSs),[33] the calculated oxidation states of Cu and V are 1.46 and 4.62, respectively. These values are close to the average oxidation states of Cu (1.33) and V (4.50) in $Ca^{2+}Cu^{2+}Cu_2^{+}(V_2^{5+}V_2^{4+})O_{12}$, indicating the existence of a mixed-valence state for Cu and V. This agrees with the experimental observation of $Ca^{2+}Cu^{2+}Cu_2^{+}(V_2^{5+}V_2^{4+})O_{12}$.[11]

The calculated elastic constants are $C_{11} = 403$ GPa, $C_{44} = 100$ GPa, and $C_{12} = 105$ GPa. This shows that $CaCu_3V_4O_{12}$ is mechanically stable because the calculated elastic constants C_{ij} satisfy the mechanical stability criteria of a cubic crystal:[34] $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, and $C_{11} + 2C_{12} > 0$. The calculated bulk modulus, shear modulus, Young's modulus, and Poisson's ratio from the Voigt−Reuss−Hill approximations[35–37] are 204, 118, and 296 GPa and 0.26, respectively. The small Poisson's ratio indicates that bonding is more directional.

For the electronic and magnetic properties, both GGA and GGA+U calculations are performed. For the GGA case, the calculated magnetic moments are −0.23 μ_B for Cu, 0.49 μ_B for V, and 0.98 μ_B for the total net magnetic moment (Table 1). This indicates that, in $CaCu_3V_4O_{12}$, Cu−V is antiferromagnetically coupled while Cu−Cu and V−V are ferromagnetically coupled. This magnetic configuration is similar to the situation in $CaCu_3B_4O_{12}$ (B = Cr, Mn, Fe).[15,16,22,25] The density of states (DOS; Figure 2a) shows that it is metallic because of the finite DOS on the Fermi level. Thus, $CaCu_3V_4O_{12}$ is a ferrimagnetic metal from the GGA calculation.

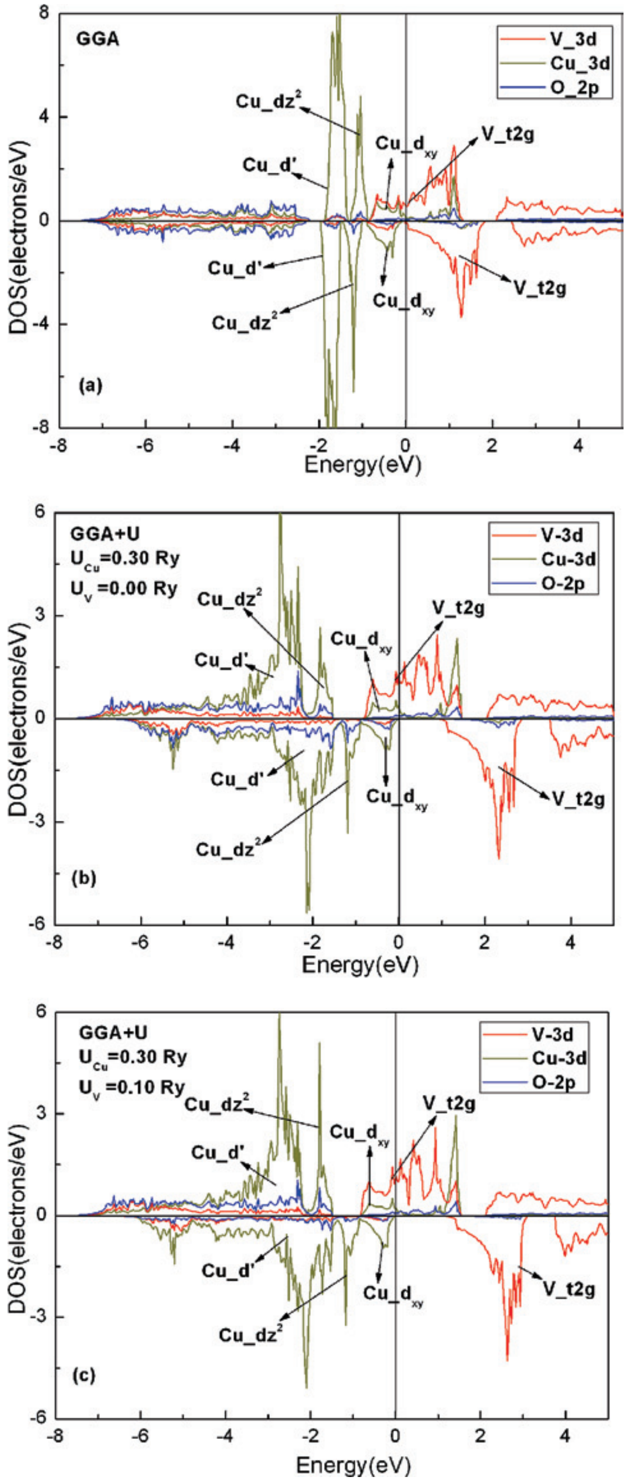

Figure 2. DOS of $CaCu_3V_4O_{12}$ from the GGA calculation: (a) without including U, (b) including U, $U_{Cu} = 0.30$ Ry, and $U_V = 0.00$ Ry, and (c) including U, $U_{Cu} = 0.30$ Ry, and $U_V = 0.10$ Ry. Cu_3d′ indicates $d_{x^2-y^2}$, d_{yz}, and d_{xz} orbitals. The energy at zero indicates the Fermi energy level.

The 3d-electron correlations (Coulomb interaction) are known to be very important for the transition-metal oxides,[38] and these electronic correlations increase as the atomic number of the transition metal increases from 22 (Ti) to 29 (Cu).[39] The importance of U was demonstrated by many studies, for instance, on the study of $CaCu_3Mn_4O_{12}$.[13] In that study,[13] LSDA+U reproduces the experimental observation that it is a semiconductor, while LSDA without U failed. Generally, GGA+U gives better results than GGA without U. This is due to the fact that the 3d electrons are strongly correlated and localized. The inclusion of parameter U will localize the electrons and thus gives more reasonable results, while GGA without U usually does not. Because the localization effect increases from Ti to Cu, parameter U has to be considered on

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Cu. Therefore, because parameter U is not included in GGA, we conducted further calculations by including the on-site Coulomb interaction U. Nonetheless, it is well-known that it is very tough to choose a reasonable U in order to reproduce the experimental data because the parameter U is system-dependent and its variation with its environment is not well understood. In general, the application of parameter U will separate the occupied and unoccupied states of the atom(s) to which it (they) is (are) applied. Thus, in some cases, as expected, a gap is produced (semiconducting), while in other cases, half-metallic behavior is observed (with a gap in the one spin direction). So, if the energy gap is available experimentally, U will be selected to fit the experimental energy gap. In the case that the energy gap is not available, like $CaCu_3V_4O_{12}$, it is hard to find a reasonable U. The parameter U is usually selected from the previous theoretical studies containing Cu and/or V. In addition, a series of U values is also necessary to find a suitable U. Therefore, in order to understand the influence of U on the magnetic and electronic properties, a series of U (U_{Cu} and U_V) values were chosen in the present study. They are (0.30, 0.0), (0.30, 0.10), (0.40, 0.20), (0.40, 0.30), (0.50, 0.30), and (0.60, 0.40). The calculated magnetic moments and energy band gaps are listed in Table 1. It can be seen that as expected, because of the enhancement of the localization effect upon increasing U values, the calculated magnetic moment and energy band gap increase. However, the calculated total net magnetic moment for each formula unit remains nearly unchanged, i.e., 1.00 μ_B (Table 1). From the calculated DOS (shown only for $U_{Cu} = 0.30$ Ry and $U_V = 0.00$ Ry at Figure 2b and $U_{Cu} = 0.30$ Ry and $U_V = 0.10$ Ry at Figure 2c (others are not shown because they have quite similar patterns), it is seen that they show quite similar behavior. The main conclusion, i.e., half-metallic and ferrimagnetic, remains unchanged. Thus, our discussion will be focused on the results from $U_{Cu} = 0.30$ Ry (4.08 eV) and $U_V = 0.00$ Ry (0.00 eV), i.e., Figure 2b. This set of values was adopted because, from previous studies, it is known that $U_{Cu} = 4.0$ eV was used in $CaCu_3Mn_4O_{12}$[13] while $U_V = 0.0$ was used in $CeVO_4$.[40]

The calculated magnetic moments are -0.49 μ_B for Cu, 0.72 μ_B for V, and 1.00 μ_B for the total net magnetic moment. These values are larger (absolute value) than the corresponding values from the GGA calculation. The calculated total net magnetic moment 1.00 μ_B is comparable to the experimental value 0.7 μ_B.[11] In addition, the DOS in Figure 2b shows that metallic behavior is observed for the spin-up channel, similar to the GGA result (Figure 2a), while for the spin-down channel, an energy gap of 1.3 eV is seen clearly. This suggests that $CaCu_3V_4O_{12}$ is half-metallic. Compared to the GGA calculation, in the spin-up channel, although the Cu d_{xy} orbital remains more or less the same, the other four Cu 3d orbitals are shifted to the lower energy region. In the spin-down channel, the significant change is the shifting of the V t_{2g} orbitals to the higher energy region, where they become unoccupied. This opens a gap in the spin-down channel and gives a half-metallic character for $CaCu_3V_4O_{12}$. This agrees with the experimental observation that $CaCu_3V_4O_{12}$ is a conductor.[11]

For the Cu 3d bands, $d_{x^2-y^2}$, d_{z^2}, d_{xz}, and d_{yz} are almost fully occupied (Figure 2b), as in other $CaCu_3B_4O_{12}$ (B = Cr, Mn, Fe).[16,22,25] This is demonstrated by the calculated integrated intensities (electron count or spin occupation) of these orbitals. For each orbital, the spin-up and spin-down channels have the same integrated intensity. For each channel (spin up or down), the calculated values are 0.92 for d_{z^2}, 0.94 for $d_{x^2-y^2}$, 0.95 for d_{xz}, and 0.95 for d_{yz}, while for the Cu d_{xy} orbital, the calculated values of the integrated intensities are 0.45 for the spin-up channel and 0.93 for the spin-down channel, suggesting that the Cu d_{xy} orbital is not fully occupied but more than half-filled. This should be an indication of the existence of 1+ Cu in $CaCu_3V_4O_{12}$; i.e., Cu should have a mixed valence of 2+ and 1+. On the other hand, for V, the calculated integrated intensities are 0.69 for the spin-up channel and 0.002 for the spin-down channel, indicating that V is also in mixed-valence states of 4+ and 5+. This is in excellent agreement with the experimental report[11] and the BVS calculations above. On the other hand, it is interesting to note that, in $CaCu_3B_4O_{12}$ (B = Cr, Mn, Fe),[16,22,25] Cu d_{xy} is only half-filled, thus making the valence of Cu only in the 2+ state.

To investigate how strong the ferrimagnetic configuration is, the exchange coupling parameter is evaluated. By forcing the spin alignment in the same direction for Cu and V, the ferromagnetic configuration is calculated to be 1637.4 meV per formula unit higher in energy than the ferrimagnetic configuration. The spin Hamiltonian is given as

$$H = \sum_{i,j} J_{i,j} S_i \cdot S_j$$

where the sum is over the pairs. By normalizing the spin vectors to unity and considering only the nearest neighbors, we obtain the exchange coupling of $J^{Cu-V} \approx 34$ meV, larger than $J^{Cu-Mn} \approx 21$ meV[15] in $CaCu_3Mn_4O_{12}$. This suggests that the Cu−V coupling in $CaCu_3V_4O_{12}$ is stronger than the Cu−Mn coupling in $CaCu_3Mn_4O_{12}$.

Conclusions

$CaCu_3V_4O_{12}$ is a ferrimagnetic, half-metallic, and mechanically stable compound. The calculated magnetic structure reveals that the coupling of Cu−V is antiferromagnteic while those of Cu−Cu and V−V are ferromagnetic. The mixed valence of Cu and V was demonstrated by the BVS calculation and the DOS. The Cu−V coupling in $CaCu_3V_4O_{12}$ is stronger than the Cu−Mn coupling in $CaCu_3Mn_4O_{12}$. The obtained results might be interesting from the viewpoint of technological applications because, in addition to the traditional use of the ferrimagnetic phase, the damage-tolerant properties may have potential applications in microelectromechanical devices.

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