Electron-correlation-induced band renormalization and Mott transition in $Ca_{1-x}Sr_xVO_3$*

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We present the local density approximate+Gutzwiller results for the electronic structure of $Ca_{1-x}Sr_xVO_3$. The substitution of Sr^{2+} by Ca^{2+} reduces the bandwidth, as the V–O–V bond angle decreases from 180° for $SrVO_3$ to about 160° for $CaVO_3$. However, we find that the bandwidth decrease induced by the V–O–V bond angle decrease is smaller as compared to that induced by electron correlation. In correlated electron systems, such as $Ca_{1-x}Sr_xVO_3$, the correlation effect of 3d electrons plays a leading role in determining the bandwidth. The electron correlation effect and crystal field splitting collaboratively determine whether the compounds will be in a metal state or in a Mott-insulator phase.

Keywords: electronic structure calculation, strongly correlated system, metal-insulator transition

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1. Introduction

The metal–insulator transition (MIT) is one of the most fundamental phenomena in condensed matter physics.[1,2] Generally, there are two kinds of MIT.[1] The first one is filling-controlled MIT, e.g., $La_{1-x}Sr_xTiO_3$[3,4] and $La_{1-x}Sr_xVO_3$.[5,6] When the divalent ion Sr^{2+} substitutes the trivalent ion La^{3+}, not only the crystal structure but also the filling electrons are modified, which leads to a complicated system. According to the Hubbard model,[2,7,8] MIT can also be controlled by varying the relative magnitudes of the on-site Coulomb repulsion U and the bandwidth W. Therefore, the second type of MIT is bandwidth-controlled MIT, e.g., V_2O_3 [9] and $Ca_{1-x}Sr_xVO_3$,[10−16] in which the filling electrons do not change, because both Sr^{2+} and Ca^{2+} are divalent ions. However, such substitution changes the V–O–V bond angle θ from 180° in $SrVO_3$ to about 160° in $CaVO_3$.[13] In the strong-ligand-field approximation, the p–d transfer interaction $t_{\rm pd}$ is scaled as $t^0_{\rm pd}\cos^2\theta$, where $t^0_{\rm pd}$ is the value for the cubic perovskite. Therefore, the bandwidth W is approximately proportional to $\cos^2\theta$. So, the bandwidth W of $Ca_{1-x}Sr_xVO_3$ can be systematically controlled without changing the number of electrons, making $Ca_{1-x}Sr_xVO_3$ one of the ideal systems for studying the bandwidth effect.[1,13]

After Fujimori *et al.*[10] reported experimental investigations of spectral and transport properties, there have been a number of papers[11−16] addressing the spectral, transport and thermodynamic properties of $Ca_{1-x}Sr_xVO_3$, yielding contradictory results. The Sommerfeld coefficient, the resistivity and the paramagnetic susceptibility do not change much with x,[11,15,17] which contradicts the widespread theoretical expectation that bandwidth W should decrease strongly with the increasing x,[13] since the V–O–V bond angle is reduced from 180° in cubic $SrVO_3$ to about 160° in orthorhombic $CaVO_3$.[18]

In $Ca_{1-x}Sr_xVO_3$, although the electrons in the narrow 3d bands are delocalized, they still show some atomic features, which are manifested in the Hubbard band and in the enhancement of the effective mass. So both local density approximation (LDA) and generalized gradient approximation (GGA) failed, as they were applied to the strongly correlated systems. To overcome the problems associated with the LDA and the GGA, the common procedure is to draw out from the LDA Hamiltonian the interaction terms for the localized orbitals, such as the 3d or 4f states, and then treat the interaction Hamiltonian explicitly in a proper way, such as the LDA+U.[19] If the interaction term is treated in the Hartree–Fock scheme, the correction over the LDA is a set of energy shifts of the local orbitals, leaving the kinetics unchanged. This is

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rational if the fluctuation effect is not strong, but it will fail in the opposite case, such as in Na_xCoO_2,[20] and LaOFeAs[21] systems and in the $Ca_{1-x}Sr_xVO_3$ system studied here. In order to study the fluctuation and the band renormalization effects, we study $Ca_{1-x}Sr_xVO_3$ using the LDA+Gutzwiller (LDA+G) method[22] in this paper.

2. Model and method

Here we briefly introduce the method used (detailed information is presented in Ref. [22]). The expectation values of the Hamiltonian in the Gutzwiller approximation and in the Hartree–Fock scheme are presented respectively by

$$\langle H\rangle_{\rm G} = \sum_{i\neq j;\sigma,\sigma'} t_{i,j}^{\sigma,\sigma'} z_{i\sigma} z_{j\sigma'} \langle C_{i\sigma}^{\dagger} C_{j\sigma'}\rangle_0 + \sum_{i;\sigma} \epsilon_{i\sigma} n_{i\sigma}^0 + \sum_{i,\Gamma} E_{i\Gamma} m_{i\Gamma}, \quad (1)$$

$$\langle H\rangle_0 = \sum_{i\neq j;\sigma,\sigma'} t_{i,j}^{\sigma,\sigma'} \langle C_{i\sigma}^{\dagger} C_{j\sigma'}\rangle_0 + \sum_{i;\sigma} (\epsilon_{i\sigma} + \Delta\epsilon_{i\sigma}) n_{i\sigma}^0 + C, \quad (2)$$

where $t_{i,j}^{\sigma,\sigma'}$ is the matrix element for the electron transfer between sites i and j with spin-orbit indices σ and σ', respectively, $z_{i\sigma}$ is the orbital-related renormalization, $C_{i\sigma}$ is the electron destruction operator, $\epsilon_{i\sigma}$ and $n_{i\sigma}^0$ are the local energy and the occupation number, respectively, $E_{i\Gamma}$ and $m_{i\Gamma}$ are the energy and the weight of configuration Γ, respectively, and $\Delta\epsilon_{i\sigma}$ is the correction to the local energy introduced by the static mean-field treatment of the interaction term.

Comparing Eq. (1) with Eq. (2), it is clear that the main difference between the Gutzwiller and the Hartree-Fock approaches is as follows. There are orbital-related factors $z_{i\sigma}$ in the former associated with the hopping terms, which describe the renormalization of the kinetic energy and the enhancement of effective mass m^*, while the kinetic energy in the Hartree–Fock approach is not renormalized. Since the enhancement of the effective mass m^* in $Ca_{1-x}Sr_xVO_3$ has been confirmed to be (2–3)m_0 by the LDA+DMFT calculation[13] and by the photoemission,[26] the thermodynamics[11,15] and the de Hass-Van Alphen experiments.[23] The above results indicate that the renormalization of the kinetic energy should be considered in the theoretical calculation.

3. Results and discussion

In this paper, we report the LDA+G results for the electronic structure of $Ca_{1-x}Sr_xVO_3$. We find that the bandwidth decrease induced by the V–O–V bond angle change is smaller than that induced by the electron correlation effect. The electron correlation energy (U) and the crystal field splitting (CF) collaboratively determine whether the compounds will be in a metal state or in the Mott-insulator phase.

Let us first discuss the band structures and the densities of states (DOS) of $SrVO_3$ and $CaVO_3$, which are shown in Figs. 1 and 2, respectively. From the LDA calculations, we can see that the O-2p states lie between -7.5 eV and -2.0 eV for $SrVO_3$ and between -7.0 eV and -2.5 eV for $CaVO_3$. In both compounds, the V ions are in an octahedral coordination of the oxygen ions, which causes the split of the V-3d states into three lower energy t_{2g} orbitals and two higher energy e_g orbitals. The t_{2g} states lie in the energy range from -1.1 eV to 1.7 eV for $SrVO_3$ and from -0.9 eV to 1.4 eV for $CaVO_3$. Such LDA results are in good agreement with previous LDA calculations.[13] However, the one-particle spectrum calculated with the LDA is poor compared with that of the experiments.[10,11,15,17,24] The main problems are: 1) The calculated bandwidth of t_{2g} is about 40% wider than the photoemission results. 2) The estimated effective mass is about 2–3 times lower than the experimental value from specific heat and susceptibility measurements.[25]

The above two problems can be well understood based on our LDA+G calculations. Here we used the Wannier function as the local orbitals with on-site Coulomb energy $U = 5.0$ eV and Hund exchange coupling $J = 1.0$ eV following the previous literatures.[10,11,15,17,24] Comparing the band structure and the DOS calculated by the LDA+G with those by the LDA, it is obvious that the bands and the DOS from -7.0 eV to -2.5 eV mostly derived from the O-2p states hardly change. However, the V-e_g states are pushed up. The most important difference between the LDA and the LDA+G are the bands of the t_{2g} orbitals, which cut across the Fermi level and are important in order to understand the properties of the compounds. From Figs. 1 and 2, we can see that the t_{2g} bands are obviously narrowed as compared with those of the LDA results. In Fig. 1 the bandwidth of t_{2g} in $SrVO_3$ reduces from 2.6 eV in the LDA to 1.6 eV in the LDA+G. That is to say, the bandwidth is reduced by about 40% compared with

that of the LDA, which agrees with the experimental results.[10,11,15,17,24] For $CaVO_3$, the bandwidth of t_{2g} reduces from 2.4 eV in the LDA to 1.3 eV in the LDA+G. It is clear that the bandwidth is reduced by about 46% compared with that of the LDA.

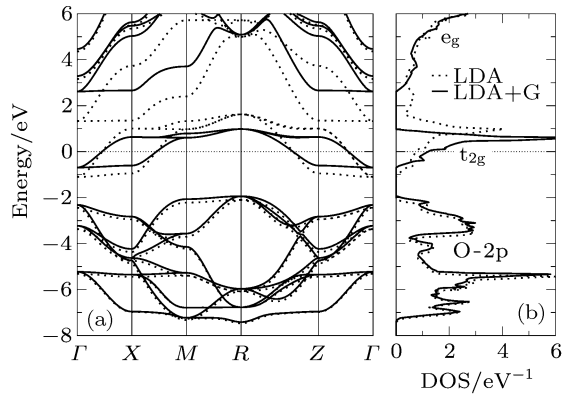


Fig. 1. (a) Calculated band structure and (b) density of state for $SrVO_3$ calculated using LDA (dashed line) and LDA+G (solid line) methods.

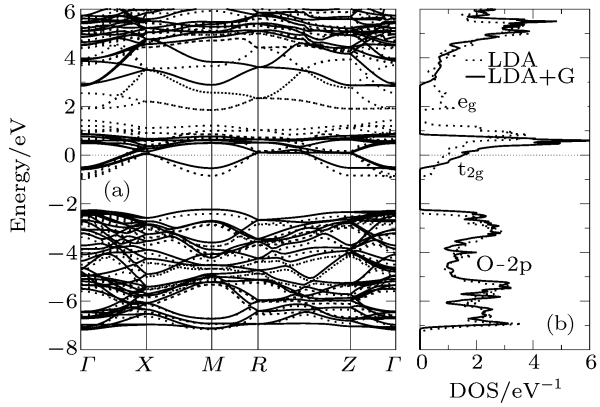


Fig. 2. (a) Calculated band structure and (b) density of state for $CaVO_3$ calculated using LDA (dashed line) and LDA+G (solid line) methods.

As mentioned above, the LDA+G results are calculated with $U = 5.0$ eV and $J = 1.0$ eV following the previous literatures. Since the on-site Coulomb energy U and the Hund's exchange coupling J are artificial parameters. It is necessary to test how the results vary with U and J. In Fig. 3, we present the calculated band renormalization factor Z^2 and the calculated bandwidth W of t_{2g} varying with U and J for both $SrVO_3$ and $CaVO_3$. It is clear that both Z^2 and W decrease quickly with the increase of U, while they increase slowly with the increase of J. Such results indicate that the on-site Coulomb energy U rather than the Hund's exchange coupling J plays the important role in determining the properties of the compounds, which is greatly different from the results in the Na_xCoO_2 system,[20] in which the Hund's exchange coupling J plays the major role. Comparing the band renormalization factors and the bandwidths between $SrVO_3$ and $CaVO_3$, we can see that both Z^2 and W of the former are smaller than those of the latter. This may be because that the V–O–V bond angle of the former is larger than that of the latter, then the bond angle decreasing further reduces the p–d transfer interaction t_{pd} and hence reduces the bandwidth of t_{2g}.

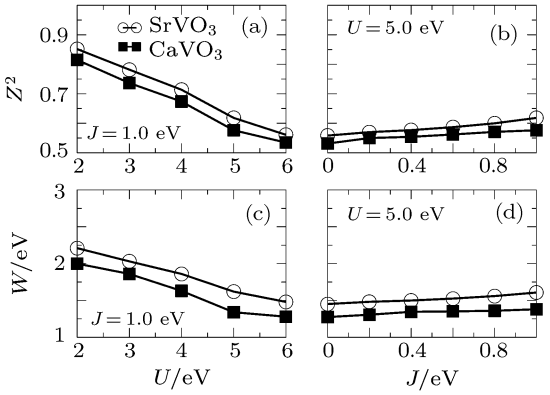


Fig. 3. Calculated band renormalization factor Z^2 ((a) and (b)) and bandwidth W ((c) and (d)) of t_{2g} for $SrVO_3$ (open circle) and $CaVO_3$ (solid square) with LDA+G method.

The substitution of large Sr^{2+} ions by smaller Ca^{2+} ions leads to the tilt and rotation of the VO_6 octahedra. Such distortions reduce the V–O_{basal}–V and the V–O_{apex}–V angles, which reduces the strength of the effective hybridization between neighboring V ions and, hence, the bandwidth. To study how the bandwidth of t_{2g} changes with the VO_6 octahedra rotation angle, we fix the VO_6 octahedra tilt angle at 161.4°, while changing the VO_6 octahedra rotation angle from 160° to 180°. Our calculations show (in Table 1) that the bandwidth of t_{2g} decreases almost linearly from 2.62 eV to 2.44 eV with the rotation angle decreasing from 180° to 160°.

Table 1. Bandwidth of t_{2g} band varying with VO_6 octahedra rotation angle.

Rotation angle/(°)	160	165	170	175	180
Bandwidth/eV	2.44	2.51	2.55	2.58	2.62

From Table 1, we can see that the bandwidth of t_{2g} decreases from 2.62 eV to 2.44 eV. Since the local Coulomb interaction of the $Ca_{1-x}Sr_xVO_3$ system is about 5.0 eV. So the ratio of U/W makes the compounds in the strongly correlated metal phase with a

quasiparticle peak at the Fermi level and the Hubbard side bands. It is widely expected that the decrease of bandwidth W will increase the ratio of U/W, then the metal-insulator transition will take place according to the Hubbard theory. Such a phenomenon actually happens in the $Sr_{2-x}Ca_xRuO_4$ system.[27−29] The substitution of the Sr^{2+} ions by the Ca^{2+} ions leads to the rotation of the RuO_6 octahedra, which reduces the bandwidth of Ru-t_{2g} accompanying the metal-insulator transition. The ideal cubic structure of $SrVO_3$ implies that the three t_{2g} orbitals (d_{xy}, d_{yz} and d_{zx}) are degenerate, because the V–O_{basal} and the V–O_{apex} distances are the same. Although the substitution of the Sr^{2+} ions by the Ca^{2+} ions splits the energy level of the t_{2g} orbitals, such smaller splitting can not result in the MIT. To seek the requirement for the MIT, we increase the V–O_{basal} distance and decrease the V–O_{apex} distance with the volume of the VO_6 octahedra fixed. So the energy level of the d_{xy} orbital will be pushed down, at the same time, the energy level of the $d_{yz/zx}$ orbital will be pushed up. Here we defined the crystal splitting (CF) as $E_{yz} - E_{xy}$, where E_{yz} and E_{xy} are the energy levels of the d_{yz} and d_{xy} orbitals, respectively. In the ideal cubic structure of $SrVO_3$, the three t_{2g} orbitals are degenerate, hence the occupation number of each orbital is 1/3. When we elongate the V–O_{basal} distance and shorten the V–O_{apex} distance, the electrons on d_{yz} and d_{zx} orbitals will transfer to the d_{xy} orbital, since the energy level of the latter one is lower than that of the former. From Figs. 4(a) and 4(c), we can see that the electron transfer increases with the CF. However, the electrons on d_{yz} and d_{zx} orbitals are not completely transferred to the d_{xy} orbital with the smaller intra-orbital action ($U < 5.0$ eV). In Fig. 4(a), when the CF is equal to 1.61 eV, more and more electrons on d_{yz} and d_{zx} orbitals are transferred to the d_{xy} orbital with the U increasing. Finally, the MIT takes place at about $U = 6.0$ eV. With smaller CF splitting, such as the CF is equal to 0.56 eV and 0.20 eV, the MIT occurs at a larger intra-orbital action, i.e., U equals to 8.0 eV and 12.0 eV, respectively. Figure. 4(d) clearly shows that the phase of the system is determined by both the CF splitting and the intra-orbital interaction.

It is well known that the intra-orbital interaction of V-3d in the VO_6 octahedra hardly changes with the chemical environment. However, the crystal field splitting between $d_{yz/zx}$ and d_{xy} can be easily controlled. If we grow $SrVO_3$ films on some special crystals with their lattice constants larger than that of the bulk $SrVO_3$, the V–O_{basal} distance will be larger than the V–O_{apex} distance. Then the CF splitting will push down the energy level of the d_{xy} orbital and cause the transfer of electrons from the $d_{yz/zx}$ orbitals to the d_{xy} orbital. When all electrons on the $d_{yz/zx}$ orbitals are transferred to the d_{xy} orbital, the MIT will take place. Actually, the MIT has been found recently in the $SrVO_3$ ultrathin films.[30]

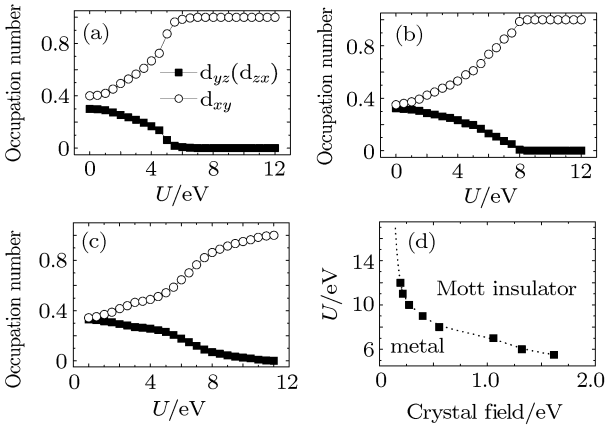


Fig. 4. Calculated occupation numbers where the CF splitting is equal to (a) 1.61 eV, (b) 0.56 eV and (c) 0.20 eV. (d)Phase diagram for the metal-Mott insulator transition. The x axis is the CF splitting and the y axis is the on-site Coulomb energy U.

4. Conclusion

In summary, based on our LDA+G calculations, we find that the bandwidth decrease induced by the V–O–V bond angle decrease is smaller than that induced by the correlation. Even with intra-orbital interaction $U = 5.0$ eV, the $Ca_{1-x}Sr_xVO_3$ system lies at the metallic state, which indicates that the compounds are a strongly correlated metal. However, if we introduce crystal field splitting by elongating the V-O_{basal} distance and shortening the V–O_{apex} distance, the electrons on the $d_{yz/zx}$ orbitals will transfer to the d_{xy} orbital, then the MIT will take place with specific intra-orbital interaction U. That is to say, the correlation effect and the CF splitting collaboratively determine whether the compounds will be in the metal state or in the Mott-insulator phase.

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