Sr$_2$(Ba$_2$)VO$_4$ under pressure – an orbital switch and potential $d^1$ superconductor

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We study Sr$_2$(Ba$_2$)VO$_4$ under high pressure by means of the local density approximation + dynamical mean field theory method. While Sr$_2$VO$_4$ is a 1/6-filling three-band system at ambient pressure with a small level splitting between the $d_{xy}$- and $d_{yz/zx}$-bands, we show that an orbital polarization occurs under uniaxial pressure, resulting in dramatic changes of the magnetic, optical, and transport properties. When pressure is applied in the $c$-direction, a $d^0$ analog of $d^0$ cuprates is realized, making Sr$_2$(Ba$_2$)VO$_4$ a possible candidate for a $d^0$ superconductor. Experimentally, this uniaxial pressure can be realized by growing Ba$_2$VO$_4$ on a substrate with lattice constant 4.1-4.2 Å.

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Since the discovery of high temperature superconductivity in cuprates$^1$, strongly correlated electron systems (SCES) and their intriguing magnetic, dielectric, optical and transport properties have been at the center of solid state research. Hence, a quantitative reliable calculation of correlation effects from first-principles is one of the most important challenges. This is particularly difficult since the standard local density approximation (LDA) in the framework of density functional theory$^2$ fails if electronic correlations are strong. Recently however, a variety of attempts which go beyond LDA have been undertaken, and many successes have been achieved$^3$.

The next step in this direction is the (theoretical) materials design of SCES with specific properties and the simulations of SCES under extreme conditions. As a touchstone for such attempts, we study the electronic structure of Sr$_2$VO$_4$ and Ba$_2$VO$_4$ under high pressure by means of the LDA+DMFT (dynamical mean field theory) method$^4$, one of the most widely used approaches for realistic calculations of SCES$^5$.

The reason why we focus on Sr$_2$VO$_4$ is twofold. First, Sr$_2$VO$_4$ is a layered perovskite, as cuprates and ruthenates$^6$ which show unconventional superconductivity. Second, the challenge to synthesize single-crystalline Sr$_2$VO$_4$ has been overcome quite recently: One of the authors and his coworkers$^7$ employed epitaxial growth techniques for growing a thin Sr$_2$VO$_4$ film. Hence, a detailed investigation of the electronic structure becomes now possible.

As for the first point, in fact, Sr$_2$VO$_4$ attracted attention because it is a ”dual” material of La$_2$CuO$_4$. Namely, the former has one 3$d$ electron per V site ($d^1$ system), while the latter has nine 3$d$ electrons per Cu site ($d^9$ system). However, as was already pointed out by Pickett et al. in 1989$^8$, there is a big difference between these oxides. While La$_2$CuO$_4$ is a 1/2-filling single-band ($d_{x^2−y^2}$) system, Sr$_2$VO$_4$ is a 1/6-filling three-band ($d_{xy}/d_{yz/ zx}$) system, since the level splitting of $t_{2g}$ in the latter material is much smaller than that of $e_g$ in the former. Therefore, the theoretical idea of unconventional superconductivity in Sr$_2$VO$_4$ has been dismissed.

Also experimentally, Sr$_2$VO$_4$ and La$_2$CuO$_4$ behave indeed differently. Magnetic properties and transport properties were measured for a polycrystal of Sr$_2$VO$_4$ in the early 1990’s$^9$, indicating that Sr$_2$VO$_4$ is an antiferromagnetic insulator (semiconductor) with a low Néel temperature $T_N$ ~ 45K. But in contrast to La$_2$CuO$_4$, a small ferromagnetic moment was also observed. In recent measurement of the optical conductivity for a single-crystalline thin film, a small gap structure, i.e., a peak around 1 eV and a shoulder around 0.5 eV was observed$^7$.

Theoretically, several first-principles calculations beyond LDA were performed, and it was confirmed that the relation between Sr$_2$VO$_4$ and La$_2$CuO$_4$ is not dual$^{10,11}$. Especially, Imai et al. carried out an LDA+PIRG (path integral renormalization group) calculation and found a nontrivial orbital-stripe order$^{10}$. These orbital degrees of freedom are irrelevant in cuprates.

The motivation of the present study is based on the following idea: While Sr$_2$VO$_4$ and La$_2$CuO$_4$ are certainly not dual at ambient pressure, we hope to change this by changing the atomic configuration of the octahedron around the V ion. Here we consider to apply high uniaxial pressure, synthesize films on substrates with appropriate lattice constant, and introduce chemical pressure (substitute Sr by Ba). If the level splitting between the $d_{xy}$ and $d_{yz/ zx}$ orbitals becomes larger, it will lead to an orbital polarization, so that the system might actually become a $d^1$ analog of $d^0$ cuprates. In this Letter, we examine this idea by means of LDA+DMFT.

GGA optimization of crystal structure. Let us now turn to our actual calculations. First, we perform a GGA (generalized gradient approximation) calculation with plane-wave basis, employing the Tokyo Ab-initio Program Package (TAPP)$^{12}$. Note that a plane-wave...
basis set has advantages for optimizing atomic configurations under high pressure which are unknown experimentally. We adopt the exchange-correlation functional introduced by Perdew et al. and ultra-soft pseudopotentials in a separable form. The wave functions are expanded up to a cut-off energy of 36.0 Ry, and 8 $k$-point grids are used. We assume that the system has the same $I4/mmm$ symmetry as at atmospheric pressure, so that there are only two free parameters, i.e., the position of the apical oxygen and Sr. In Fig. (a), we show the atomic configuration of the octahedron around the V ion.

We calculate the total energy as a function of the lattice constant $a$, fixing the ratio $c/a$ to its experimental value ($=3.28$). We find that the energy minimum is at $a=3.89$Å (not shown), in excellent agreement with experiment ($a=3.84$Å). When the lattice constant $a$ is fixed to this optimized value, the Sr-V and O-V distances along the $c$-direction become 4.46Å and 2.01Å, respectively, consistent with the experimental values 4.46Å and 1.98Å.

Next, we change the lattice constants to simulate the effect of pressure. Considering to apply high uniaxial pressure or, more realistically, to synthesize Sr$_2$VO$_4$ films on substrates with appropriate lattice constant, we change the lattice constant $c$ up to $\pm 10\%$ of the experimental value $c_0=12.76$Å.

In Fig. (b), we plot the GGA-optimized distance between O and V along the $c$-direction ($d_{c}$) and within the $ab$-plane ($d_{ab}$) as a function of $c/c_0$. Here we fix the volume of the unit cell ($V$) rather than $a$, since the total energy at fixed $V$ is always lower than that of fixed $a$. While the V-O distance $d_c$ is longer than $d_{ab}$ at ambient pressure, $d_c$ becomes shorter than $d_{ab}$ for $c/c_0 < 0.95$.

In fact, the ratio $d_c/d_{ab}$ determines the splitting of the three $t_{2g}$ orbitals. If we press uniaxially along the $c$-direction, the negatively charged oxygen ions move towards the vanadium site. Hence the energy of the $d_{yz}/d_{xz}$ orbitals, which point along the $c$-direction, is enhanced. At ambient pressure the level splitting is small. But given the fact that $d_c$ and $d_{ab}$ change considerably with $c/c_0$ in Fig. (b), we may expect that we can control the level splitting, and, consequently, the orbital occupation by applying pressure.

**LDA+DMFT calculation.** To examine this idea in the presence of electron correlations, we perform LDA+DMFT calculations for the atomic configurations obtained above. To this end, we first carry out LDA band structure calculations with the LMTO (linearized muffin tin orbital) basis. In the inset of Fig. 2 we show the obtained band structure for ambient pressure. Almost the same band structure is obtained by the GGA calculation with plane-wave basis.

Then, we extract the three $t_{2g}$ bands by the NMTO (N-th order muffin tin orbital) downfolding, using the generated LDA potential. As a typical example of the resulting NMTO Wannier functions, we show the $d_{xy}$-orbital of V in Fig. (a) for ambient pressure. The density of states (DOS) of the $t_{2g}$ band for $c/c_0 = 0.9$, 1.0 and 1.1 are shown in Fig. 2. The NMTO band width of the $d_{xy}$-band is 2.46 eV at ambient pressure ($c = c_0$). This value is consistent with that of the GGA calculation with plane-wave basis and that of Pickett et al. who used the full-potential linearized augmented plane wave (LAPW) basis. Imai et al.

For the case of $c/c_0=0.9(1.1)$, Fig. 2 shows that the center of gravity of the $d_{yz}/d_{xz}$-bands is clearly higher(lower) than that of the $d_{xy}$-band. Indeed, the crystal field splitting between the $d_{xy}$- and $d_{xz}/d_{yz}$-orbitals in the NMTO Hamiltonian is $-382(+434)$ meV for $c/c_0=0.9(1.1)$. Concerning the electron occupation of the $d_{xy}$- and $d_{xz}/d_{yz}$-orbitals, 90% (20%) of the $d$ electrons
the other hand, Sekiyama et al. estimated smaller Coulomb interactions: $U' \sim 1.3$ and $J \sim 0.65$ eV by the combination of the constrained LDA and the GW method[10]. However, as mentioned above, the band width of the $t_{2g}$-orbitals of Ref. [10] is 20-25% smaller than that of the present study. If we normalize the interaction parameters by the band width, the difference is not so big. On the other hand, Sekiyama et al. employed $U' = 3.55$ and $J = 1.0$ eV in their LDA+DMFT calculation for SrVO$_4$, reproducing the photoemission spectrum of SrVO$_4$[21]. These values are not so far from ours.

Let us now turn to the LDA+DMFT results for high pressure. In Fig. 4(a), we plot the spectral function for $c/c_0 = 1.1$, showing a metallic peak at the Fermi level. In contrast to ambient pressure, there is no coexisting insulating solution at $c/c_0 = 1.1$, i.e., applying pressure in the ab plane makes Sr$_2$VO$_4$ metallic. An important point is that the $d_{xy}$-orbital is almost empty for $c/c_0 = 1.1$: orbital polarization occurs. The system becomes a quarter-filled 2-band Hubbard model which is well known to have a ferromagnetic ground state[22, 23]. Therefore, we expect ferromagnetic spin fluctuation to be dominant at low $T$ if pressure is applied in the ab plane.

On the other hand, Fig. 4(b) shows the result for uniaxial pressure along the c direction ($c/c_0 = 0.9$). We see that the spectrum is now clearly insulating, even for the smaller value of $U' = 2.5$ for which we have a metal in Fig. 3(a). This is a surprising result: an inverse Mott-Hubbard transition. (Usually, applying pressure makes an insulator metallic, not a metal insulating as from Fig. 3(a) to Fig. 3(b).) What is the reason for this unusual behavior? From Fig. 3 we see that the LDA band width does not change strongly from 2.26 eV at $c/c_0 = 1$ to 2.46 eV at $c/c_0 = 0.9$. This small change of band width alone would indeed indicate more metallic behavior—as usual. But more important is that uniaxial pressure changes the crystal-field splitting: The two $d_{yz/zx}$-orbitals become unoccupied, and then the large intra-orbital repulsion $U$ makes the remaining (single) $d_{xy}$-orbital Mott-insulating. This way, a $d^1$ analog of $d^9$ cuprates is realized. Concerning the magnetic properties, we expect an antiferromagnetic instability since the system becomes a half-filled single-band model.

$BaVO_4$. While it is an interesting possibility to change the electronic properties by controlling the lattice constant, it might be difficult to change its value up to $\pm 10\%$. For example, in order to grow Sr$_2$VO$_4$ thin films with $c/c_0 = 0.9$, we need considerably large lattice mismatch between a substrate and bulk Sr$_2$VO$_4$, while an excessive mismatch often results in lattice relaxation.
The electron density is 0.73 for the d band. Thus, lastly, we consider the possibility of chemical pressure by substituting Sr by Ba. Since the ion radius of Ba is larger than that of Sr, the crystal is expected to be expanded. The important point here is that the V-O distance in the ab plane and that along the c axis will increase differently. Namely, while the increase of c directly affects the V-O distance in the ab plane (the latter is exactly half of the former), c and the V-O distance along the c axis are independent parameters.

First, we perform GGA calculation with structure optimization for Ba$_2$VO$_4$ by changing a and c. The energy minimum is at $a = 4.04$ Å and $c/a = 3.36$, the V-O distances are 2.02 Å in the ab plane (compared to 1.92 Å for Sr$_2$VO$_4$) and 2.01 Å along the c direction (2.01 Å for Sr$_2$VO$_4$). This means that the situation for Ba$_2$VO$_4$ is similar to that of Sr$_2$VO$_4$ with $c/c_0 = 0.95$, i.e., if uniaxial pressure is already applied.

Next, we consider the compression $c/c_0 = 0.95$ for Ba$_2$VO$_4$. The orbital polarization becomes larger, i.e., the electron density is 0.73 for the $d_{xy}$ band and 0.14 for the $d_{yz/zx}$ band. Thus it is interesting to proceed with DMFT calculations. In Fig. 5, we plot the resulting LDA+DMFT spectral function for ambient pressure and uniaxial pressure in the c direction ($c/c_0 = 0.95$) with $U' = 2.5$, along with the density of states by LDA. We can see that a large orbital polarization is realized even for $c/c_0 = 0.95$. Since the relative hopping and interaction parameters for the $d_{xy}$ band are very similar to the cuprates, a $d^1$ analog of $d^9$ cuprates can be realized. Experimentally, the uniaxial pressure is best realized by growing Ba$_2$VO$_4$ on a substrate with a larger in-plane lattice constant 4.1-4.2 Å.

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