Pressure-Induced Restoration of the Reversed Crystal-Field Splitting in $\alpha$-Sr$_2$CrO$_4$

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Motivated by an experimental finding that the successive phase transitions in $\alpha$-Sr$_2$CrO$_4$ observed at ambient pressure ceases to exist under high pressures, we carry out the density-functional-theory-based electronic structure calculations and demonstrate that the reversal of the crystal-field splitting reported previously is restored under high pressures, so that the orbital degrees of freedom disappears, resulting in the single phase transition that divides the system into high-temperature Mott insulating and low-temperature antiferromagnetic insulating phases.

KEYWORDS: Sr$_2$CrO$_4$, crystal field splitting, orbital ordering, pressure effect

1. Introduction

The orbital degrees of freedom in transition-metal compounds have long been one of the major themes in the physics of strongly correlated electron systems [1]. One of the recent examples is the origin of successive phase transitions observed in a layered perovskite $\alpha$-Sr$_2$CrO$_4$ [2]. This material is a Mott insulator, having the K$_2$NiF$_4$-type crystal structure with CrO$_6$ octahedra elongated along the c-axis of the lattice and with a $3d^2$ electron configuration [3, 4]. Therefore, one would naturally expect that two electrons occupy the lowest doubly degenerate $t_{2g}$ orbitals forming an $S = 1$ spin due to Hund’s rule coupling, so that only the antiferromagnetic Néel ordering of $S = 1$ spins occurs below the Néel temperature $T_N$, without any orbital ordering. However, a recent experimental study [2] revealed that two phase transitions occur successively at 112 and 140 K, releasing nearly the same amount of entropy. The lower-temperature phase transition (denoted as $T_N$) was ascribed to Néel ordering by magnetic measurement, but the cause of the higher-temperature one (denoted as $T_S$) remained a mystery from the experiment [2, 5, 6].

Then, using the density-functional-theory (DFT) based electronic structure calculations, Ishikawa et al. [7] have shown that the crystal field level of nondegenerate $3d_{xy}$ orbitals of
Cr ion is in fact lower in energy than that of doubly degenerate $3d_{yz}$ and $3d_{xz}$ orbitals, giving rise to the orbital degrees of freedom in the system with a $3d^2$ electron configuration. Thereby, they have argued that the higher (lower) temperature phase transition is caused by the ordering of the orbital (spin) degrees of freedom of the system. Because the CrO$_6$ octahedron is elongated along the $c$-axis of the crystal structure, this result offers a rare example of the reversal of the crystal-field splitting in transition-metal compounds.

A natural question that arises in this respect would then be what occurs if external pressures are applied to this system. Recently, Yamauchi et al. [8] reported that the successive phase transitions disappear at a high pressure above a few GPa, leaving only one phase transition that divides the system into two phases, a high-temperature paramagnetic insulating phase and a low-temperature antiferromagnetic insulating phase. This result can readily be understood if we assume that the reversal of the crystal-field splitting ceases to occur under high pressures, so that the lowest doubly degenerate $t_{2g}$ orbitals are occupied by two electrons, forming an $S = 1$ spin due to Hund’s rule coupling, which leads to the antiferromagnetic Néel ordering of $S = 1$ spins at $T_N$, without any orbital ordering.

In this paper, to check the validity of this assumption, we apply the DFT-based electronic structure calculations using the generalized gradient approximation (GGA); in particular, we use the GGA+$U$ method for a better description of electron correlations. We thus show that the reversed crystal-field splitting in $\alpha$-Sr$_2$CrO$_4$ is actually restored under high pressures, resulting in the elimination of the orbital degrees of freedom of the system.

2. Computational details

We employ the WIEN2k code [9] based on the full-potential linearized augmented-plane-wave method for our DFT calculations. Here, we present results obtained in the GGA for electron correlations using the exchange-correlation potential of Ref. [10]. To improve the description of electron correlations in the Cr $3d$ orbitals, we also use the rotationally invariant version of the GGA+$U$ method with the double-counting correction in the fully localized limit [11, 12]. In particular, we examine the $U$ dependence of the crystal-field splitting. The spin polarization is not allowed in the present calculations. The spin-orbit interaction is not taken into account. We use the crystal structure measured at high pressures [8], which has the tetragonal symmetry (space group $I4/mmm$) with one (two) crystallographically inequivalent Cr (O) ions, but we apply the local structural relaxations keeping the measured lattice constants unchanged. We assume the high-temperature metallic phase, allowing for no antiferromagnetic spin polarizations. In the self-consistent calculations, we use 99 $k$-points in the irreducible part of the Brillouin zone. Muffin-tin radii ($R_{MT}$) of $\sim 2.3$ (Sr), $\sim 1.9$ (Cr), and $\sim 1.7$ (O) Bohr depending on pressures are used and a plane-wave cutoff of $K_{\text{max}} = 8.00/R_{MT}$ is assumed.

3. Results of calculation

The calculated energy dispersions of the three bands near the Fermi level are fitted by the tight-binding bands of the three molecular orbitals obtained as the maximally localized Wannier functions [13, 14]. The energy-level splittings of the maximally localized Wannier
Fig. 1. Calculated splitting $\Delta E_{xy-yz} = E(d_{xy}) - E(d_{yz})$ of the energy levels of the maximally localized Wannier orbitals as a function of applied pressure $P$, where several $U$ values are assumed in the GGA+$U$ calculations.

orbitals are thus determined as a function of the applied pressure.

Then, our calculated results for the crystal-field splitting are given in Fig. 1, where we present the pressure dependence of the difference in the energy levels between the nondegenerate $3d_{xy}$ orbital and the doubly degenerate $3d_{yz}$ and $3d_{xz}$ orbitals of a Cr ion, i.e., $\Delta E_{xy-yz} = E(d_{xy}) - E(d_{yz})$. Here, we first confirm that the reversal of the crystal-field splitting, $E(d_{xy}) < E(d_{yz}) = E(d_{xz})$, actually occurs at ambient pressure, as was found in Ref. [7]. Then, under high pressures $P \gtrsim 2$ GPa, we find that the reversal of the crystal-field splitting is restored, i.e., $E(d_{xy}) > E(d_{yz}) = E(d_{xz})$, in particular when we assume the standard value of $U = 3$ eV for Cr ion. We should note that the restoration of the reversed crystal-field splitting occurs only for larger values of $U$ ($\gtrsim 3$ eV), which means that the restoration is not a simple pressure effect but rather the cooperation with $U$ is essential. Thus, the effect of strong electron correlations is suggested to be important in $\alpha$-Sr$_2$CrO$_4$, as was noticed in Ref. [7]. More precisely, the repulsive interaction $U$ in the GGA+$U$ type of approximations in general works to lower (raise) the energy of the occupied (unoccupied) orbitals [12,15]. In the present case, the interaction $U$ works to stabilize the state where the doubly degenerate orbitals ($d_{yz}$ and $d_{xz}$) are occupied by two electrons, in comparison with the state where the nondegenerate $d_{xy}$ orbital is occupied by two electrons.

Thus, we have shown that the reversed crystal-field splitting in $\alpha$-Sr$_2$CrO$_4$ is actually restored under high pressures, resulting in the elimination of the orbital degrees of freedom of the system, which naturally leads to the single phase transition that divides the system into two phases, a high-temperature paramagnetic Mott insulating phase and a low-temperature antiferromagnetic insulating phase, in agreement with experiment [8]. Note that, in the present calculation, the paramagnetic metallic state without antiferromagnetic spin polarization is assumed for extracting the values of the crystal-field splitting because the paramagnetic Mott insulating state cannot be obtained in the GGA+$U$ type of calculations.
However, the present assumption is usually sufficient for extracting the values because they are not strongly affected by the spin polarization of the system [7].

4. Summary

In our previous paper [7], we have shown that the successive phase transitions observed in a layered perovskite $\alpha$-Sr$_2$CrO$_4$ at ambient pressure are ascribed to the active orbital degrees of freedom of the system caused by the reversal of the crystal-field splitting of the system. However, a recent high-pressure experiment [8] has shown that the successive phase transitions disappear under high pressures, leaving only one phase transition dividing the system into two phases, a high-temperature paramagnetic insulating phase and a low-temperature antiferromagnetic insulating phase.

Motivated by this experimental finding, we have made the DFT-based electronic structure calculations for $\alpha$-Sr$_2$CrO$_4$ under high pressures in the GGA+$U$ method and have demonstrated that the reversal of the crystal-field splitting is actually restored under high pressures, so that the orbital degrees of freedom of this system disappears, resulting in the single antiferromagnetic phase transition.

Our result for $\alpha$-Sr$_2$CrO$_4$ on the one hand provides an interesting example of the pressure effects in strongly-correlated transition-metal compounds, but on the other hand reinforces the idea that the reversal of the crystal-field splitting found in $\alpha$-Sr$_2$CrO$_4$ is a rare and fragile phenomenon easily destroyed by the external perturbation.

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