Electronic structure of Cr-doped SrRuO₃: Supercell calculations

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The effects of partial Cr substitution for Ru in SrRuO₃ are studied using supercell calculations. We find a strong tendency towards antiparallel alignments of Ru and Cr moments resulting from hybridization between Cr t_{2g} orbitals and spin-polarized O states near the Fermi energy. The resulting strong local exchange interaction provides an explanation for the increase in the Curie temperature of SrRuO₃ when alloying with Cr.

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I. INTRODUCTION

SrRuO₃ is of interest both because it is practically the only example of a robust 4d ferromagnetic metal and because of the wide variety of physical ground states observed in related Ru⁴⁺-perovskite-derived ruthenates. These include metamagnetic quantum criticality in Sr₃Ru₂O₇,¹ unconventional, possibly spin-fluctuation-induced, superconductivity in Sr₂RuO₄,^{2,3} and giant magnetotransport effects in Ca₃Ru₂O₇.⁴⁻⁷ A particular challenge is to connect the properties of the various ruthenate phases. One way to approach this is via alloying studies. Alloying on the divalent A site allows a connection of the Sr- and Ca-based phases and has revealed a rich variety of phases—e.g., in the (Sr,Ca)₂RuO₄ system.⁸ Doping on the Ru site generally has strong effects on the properties. For example, even small amounts of Ti induce magnetic behavior in the paramagnetic superconducting phase, Sr₂RuO₄.⁹⁻¹²

As mentioned, SrRuO₃ is a ferromagnetic metal.¹³⁻¹⁶ The very high magnetocrystalline anisotropy, which results from the strong spin-orbit interaction on the 4d magnetic ion, and the normally twinned, orthorhombic nature of the material complicate magnetic measurements.^{14,15,17} However, accepted values of the Curie temperature and magnetization are $T_C = 165$ K and $M = 1.6\mu_B/\text{Ru}$.¹⁸ Standard density functional calculations, within the local density approximation, have been shown to reproduce this value of the magnetization and other properties.^{16,19} According to these calculations, SrRuO₃ is an itinerant ferromagnetic metal, with strong magnetoelastic coupling. The magnetism arises from a Stoner instability, which in turn results from a high density of states derived from Ru t_{2g} —O p —hybridized bands around the Fermi energy E_F . A remarkable feature of ruthenate magnetism is that O p states are heavily involved. Only $\sim 2/3$ of the magnetization is Ru d derived—the remaining $\sim 1/3$ is on O.^{16,20} This is due to the strong hybridization between Ru and O (note that 4d orbitals are much more extended than 3d orbitals).

SrRuO₃ has been doped with a number of elements.²¹⁻²⁷ Pi and co-workers²¹ also studied the effect of creating vacancies on the Ru site, as in SrRu_{1-x}O₃ (vacancies on the perovskite B site), and found decreased T_C . In all cases, except Cr and Pb, T_C is lowered, usually quickly. For Cr doping, T_C increases strongly with Cr content, reaching 188 K.^{21,22,24-27} Furthermore, Cr doping of paramagnetic CaRuO₃ was shown

to produce a ferromagnetic state.²⁸ Besides the fundamental interest in understanding magnetism in ruthenates and 4d oxides, there is a practical motivation. In particular, a room-temperature 4d oxide magnet would be useful because of the large spin-orbit interaction, which would be expected to yield, e.g., very large magnetocrystalline anisotropy and Kerr rotation. Here we report density functional calculations for SrRu_{1-x}Cr_xO₃ supercells and use these to elucidate the electronic structure and magnetic coupling of Cr substitutionals in SrRuO₃.

II. APPROACH

A supercell approach was used to model Cr substitutions in SrRuO₃. Two supercells were constructed. The first was constructed by substitution of one Ru by Cr within the orthorhombic *Phnm* structure unit cell of SrRuO₃. This unit cell contains four Ru per $\sqrt{2} \times 2 \times \sqrt{2}$ unit cell.²⁹ This corresponds to 25% Cr substitution and has no Cr-Cr nearest-*B*-site-neighbor pairs. Therefore there are no Cr-O-Cr bonds, and breathing of the CrO₆ octahedra can occur. The cell contains three inequivalent Ru atoms: Ru(1) with four Cr neighbors and two Ru neighbors, Ru(2) with two Cr neighbors and four Ru neighbors, and Ru(3) with six Ru neighbors. The second cell is a doubled cell, $2 \times 2 \times 2$, with respect to a five-atom perovskite cube. This cell was based on a doubling of the experimental structure of SrRuO₃, again with one Ru replaced by Cr, corresponding to 12.5% Cr substitution. Like the smaller supercell, this cell has no Cr-O-Cr bonds. In addition, all the Ru ions have either six Ru nearest *B*-site neighbors or two nearest *B*-site Cr neighbors with four Ru neighbors.

The calculations reported here were performed within the local spin density approximation (LSDA), based on the electron gas fit of Perdew and Wang,³⁰ using the general potential linearized augmented plane-wave (LAPW) method,³¹⁻³³ as implemented in the WIEN2k program.³⁴ We also repeated some calculations with an independent LAPW code employing an LAPW plus local orbital basis set, but did not find any significant differences in the results. This method is well suited to treating open structures with low site symmetries and in particular makes no shape approximations to the potential or charge density and has a flexible basis both in the interstitial and near the atomic centers. The core states were

TABLE I. Cr moments as measured by the spin magnetization inside the Cr LAPW spheres (radius $2.0a_0$) for F and AF alignments in the various supercells (rel denotes relaxed) and the energy difference between the F and AF configurations. Positive energy differences ΔE mean that the AF configuration is lower in energy.

	$m(\text{F}) (\mu_B)$	$m(\text{AF}) (\mu_B)$	ΔE (mRy)
25%	1.94	-1.99	13
25% (rel)	1.76	-1.85	15
12.5%	1.91	-2.00	14

treated relativistically, while the valence states were treated in a scalar relativistic approximation.

As mentioned, spin-orbit is important for some physical properties of SrRuO_3 —for example, the magnetocrystalline anisotropy. In order to verify that the scalar-relativistic approximation used here is valid for the results presented, we did calculations including spin-orbit for one of the supercells. Specifically, we did self-consistent calculations including spin-orbit in a second variational step for the unrelaxed 25% Cr supercell (see below). We found that the energy difference between Cr moments parallel and antiparallel to the SrRuO_3 host magnetization changed by 0.2 mRy, in favor of the antiparallel case. This is compared with the total energy difference between these two configurations of 13 mRy.

LAPW sphere radii of $0.2a_0$ and $1.6a_0$ were used for the metal and O atoms, respectively. We employed well-converged basis sets, defined by $R_{\min}K_{\max}=7.0$, where $R_{\min}$ is the O LAPW sphere radius and $K_{\max}$ is the interstitial plane-wave cutoff. Local orbitals were employed, both to include semicore states and to efficiently linearize the Ru d and O s and p states.³³

We calculated the electronic structures, total energies, and forces for both supercells, with the Cr moment parallel to the Ru magnetization (denoted F in the following) and antiparallel (denoted AF), with the lattice parameters and atomic coordinates constrained to be identical to those of $Pbnm$ SrRuO_3 .²⁹ The calculated forces were small. The maximum force was an inward force on the O comprising the CrO_6 octahedra, of 0.023 Ry/ a_0 . We also did structural relaxations of all internal coordinates of the 25% Cr supercell with both F and AF Cr moment alignments, but the changes in magnetic energies and electronic structure were small, as discussed below.

III. MAGNETISM

The Cr moments, as measured by the spin polarizations inside the Cr LAPW spheres and the calculated energy differences between F and AF Cr alignments, are given in Table I. Total spin magnetizations of bulk SrRuO_3 and the supercells are given in Table II, on a per transition element atom basis. As may be seen the Cr moments in the LAPW spheres are only weakly dependent on the magnetization direction with respect to the host lattice and the energy scale between F and AF alignment is very high compared to the magnetic

TABLE II. Calculated spin magnetization in μ_B of bulk SrRuO_3 and the supercells, on a per transition metal atom (Ru and Cr) basis, as in Table I.

	M (F)	M (AF)
Bulk	1.59	
25%	1.70	0.79
25% (rel.)	1.53	0.81
12.5%	1.56	1.19

energy scales in the undoped ruthenate. For comparison, the LSDA total magnetic energy for SrRuO_3 , defined as the difference between a constrained non-spin-polarized solution and the ferromagnetic ground state, is ~ 4 mRy/Ru. This high-energy scale reflects a strong spin-dependent hybridization between Cr and the host lattice, as discussed below. It also explains the rapid increase of T_C with Cr doping. $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$ shows a monotonic concave downwards increase in T_C at least up to $x=0.15$, with an initial slope of $\frac{dT_C}{dx} \sim 280$ K—i.e., 2.8 K/at. % Cr.²⁴

In the simplest nearest-neighbor picture for a simple cubic (perovskite) topology, replacing the exchange constant coupling dilute randomly placed Cr ions to their neighboring Ru by large, effectively infinite, values, of either sign, will stiffen the low- q magnons according to $J_{\text{eff}}(x)=(1+2x)J_{\text{eff}}(0)$, where the factor of 2 arises because each bond is shared by two atoms and where the magnon wavelength remains longer than the average Cr-Cr spacing corresponding to the concentration x . This formula is just the expression for the stiffness of a string of torsion springs, where a portion $2x$ of the springs have been replaced by rigid links. In any case, since the scale of T_C is set by J_{eff} , this simple picture would yield $\frac{dT_C}{dx}=2xT_C(0)=330$ K, which is remarkably close to the observed value of 280 K, especially considering that the exchange coupling between the Cr moment and the host is large, but not infinite, and that there are changes in the host electronic structure, as well (see below). This picture will break down when the x reaches the level where there are significant numbers of Cr-Cr neighbors. It is interesting that when extrapolating the data of Ref. 24 for $0 \leq x \leq 0.15$, T_C appears to be approaching saturation a little beyond 0.15, while the number of B -site near neighbors in perovskite is 6 (note $1/6 \sim 0.17$).

IV. ELECTRONIC STRUCTURE

The three supercells (25%, relaxed and unrelaxed, and 12.5% unrelaxed) had similar energetics for the Cr magnetism and the relevant features of the electronic structure, discussed below. However, since the effect of the relaxation was small, we focus on the 12.5% Cr supercell in the following, since this is within the range of experimentally realized Cr concentrations with $Pbnm$ crystal structure.

The total electronic densities of states (DOS) and projections onto LAPW spheres for the 12.5% Cr supercell with F and AF alignments are shown in Figs. 1 and 2, respectively. The shapes of the DOS for the smaller 25% Cr cell are simi-

FIG. 1. (Color online) Total and projected DOS for the ferromagnetic (F) 12.5% Cr supercell. The projected DOS for Ru and O spheres are separated into two types. Here “cage” refers to the six sites that form the octahedral O and B-site cages around the Cr atom and “other” refers to the other, more distant sites.

lar and are not shown. The projections onto Ru and O are divided into two types: those from the six nearest to the Cr and farther sites. As may be seen both the Ru- and O-projected DOS away from the Cr are quite bulk like and independent of the Cr moment direction. The mechanism for the strong coupling between the Cr moment and the host

FIG. 2. (Color online) Total and projected DOS for the antiferromagnetic (AF) 12.5% Cr supercell. The projected DOS for Ru and O spheres are separated into two types. Here “cage” (dashed line) refers to the six sites that form the octahedral O and B-site cages around the Cr atom and “other” (solid line) refers to the more distant sites.

magnetization is seen by comparing the F and AF projections of the DOS.

In an octahedral crystal field, the d levels are split into a lower-lying three fold-degenerate (per spin) t_{2g} manifold and a higher two fold-degenerate e_g manifold. These levels are then exchange split, forming moments on the Cr. As may be seen from the DOS, the Cr exchange splitting is ~ 1.5 eV, and in both cases E_F occurs in the Cr majority-spin t_{2g} peak, while the minority t_{2g} peak starts above E_F . Thus the Cr valence is clearly different from Cr^{3+} .

As mentioned, in SrRuO_3 there is strong covalency between the Ru d and O p states, leading to an electronic structure near E_F comprised of hybridized bands. Both the Ru d and O p states are therefore exchange split, but roughly the same amount, with the result of substantial moments on the O sites and significant O contributions to the magnetic energy. The ferromagnetism is associated with an asymmetric DOS peak near E_F , which falls off quickly to higher energy, but has a slower decay going to lower energy. Thus, when exchange split, almost all of the states making up the peak become occupied in the majority-spin channel. However, in the minority channel, while the maximum in the DOS moves above E_F , there remains considerable DOS below E_F (see Ref. 16). The same structure is seen from -2 eV to 1 eV in the total DOS of Figs. 1 and 2. Like Ru, Cr can have different valence states, and Cr oxides can be magnetic and metallic, as in, e.g., CrO_2 . Common valence states of Cr are Cr^{3+} , Cr^{4+} , and Cr^{6+} . The occurrence of Cr^{4+} would be consistent with local electrostatic neutrality, while Cr^{3+} has an ionic radius that very close to that of Ru^{4+} ,³⁵ and therefore might be favored by considerations of local strain effects.

The calculated Cr projections of the DOS show that the majority t_{2g} orbitals are partly occupied, while the minority t_{2g} orbitals are unoccupied. An estimate of the d occupation can be made by integrating the peak associated with the t_{2g} orbitals. We find that for the lowest-energy AF ordering, in the 12.5% Cr supercell, the occupied fraction of the peak is 0.76, corresponding to an electron count of $2.3e$ —i.e., intermediate between Cr^{3+} and Cr^{4+} , but closer to Cr^{4+} . We note that this is for the unrelaxed structure.

The exchange splitting in bulk SrRuO_3 depends somewhat on the band in question because of the Ru d -O p hybridization. For the states near E_F it is $\Delta_{ex} = 0.65$ eV for the equilibrium magnetization of $1.59\mu_B$ (Ref. 16), and in view of the near-rigid splitting of the t_{2g} peak near E_F that underlies the magnetic instability, Δ_{ex} will be proportional to the magnetization. This is qualitatively what is seen in the projected density of states for the supercell in relation to the moments on the cage and other Ru sites (Table III).

As mentioned, the forces on the O making the CrO_6 are small and directed towards the Cr. This would favor a valence still closer to Cr^{4+} if relaxation were allowed. In fact, this is what we find in the relaxed 25% supercell. Specifically, we relaxed all the internal atomic positions in the 25% supercell for F and AF Cr alignments. We found only a small change in the energy difference, which was increased from 13 mRy to 15 mRy. The main structural difference upon relaxation was a reduction in the average bond Cr-O bond length in the CrO_6 octahedra by 0.03 Å. When measured, as above, using the Cr d projection of the DOS, the filling of the

TABLE III. Calculated spin moments on Ru and O sites in the 25% supercells, relaxed (rel) and unrelaxed (unrel), with F and AF Cr alignment. The moments are given in μ_B and defined as the projections of the spin density within the LAPW spheres (see text) and are averaged over cage (nearest six neighbors to Cr, denoted “cage”) and more distant sites (denoted “other”).

Site	FM(unrel)	FM(rel)	AF(unrel)	AF(rel)
Ru(cage)	0.89	0.94	1.19	1.17
Ru(other)	1.02	0.90	0.90	0.94
O(cage)	0.14	0.13	0.13	0.14
O(other)	0.07	0.07	0.09	0.08

Cr t_{2g} manifold decreases from $2.3e$ (the same as in the 12.5% cell) to $2.1e$. Thus the Cr valence is closer to Cr^{4+} than to Cr^{3+} , even though the Cr-O bond lengths are relatively long. The explanation is apparently the strong Cr-O hybridization in this compound. In fact, as may be seen from the projected DOS, there is substantial Cr d character in the low-energy part of the O p bands, which corresponds to the formation of e_g-p_σ hybrid bands. Again, by integration of the Cr d projections of the DOS from the bottom of the O $2p$ bands to -2 eV and from just above the t_{2g} peak to 6 eV, we obtain an estimate of $0.8e_g$ electrons in the occupied bands. In any case, like Ru, there is strong Cr d -O p hybridization, but there is apparently little charge transfer between the Cr and the ruthenate host. We note that hole-doping of SrRuO_3 by partial substitution of Sr by Na strongly suppresses ferromagnetism.³⁶ If band filling were the key parameter, then substitution of a trivalent B -site ion might also be expected to suppress ferromagnetism contrary to what is observed for Cr doping.

For AF alignment, the energy position of the partly occupied majority-spin Cr t_{2g} (this is the spin-down direction for this alignment) states matches the hybridized Ru-O states in the host minority spin. The result is a broadening of the majority-spin (spin-down) Cr t_{2g} peak, as seen in the Cr d projection. This broadening lowers the energy because the Cr t_{2g} level is partially filled. The projected DOS for the F alignment shows a much narrower majority-spin (now spin-up) Cr t_{2g} manifold. This is because the O levels with which it would hybridize are mostly lower in energy and fully occupied. Thus the mechanism for the strong antiferromagnetic coupling of the Cr moments to the host lattice is strong hybridization between spin-polarized Cr t_{2g} orbitals and spin-polarized O p orbitals associated with the Ru t_{2g} -O p_π band structure near E_F .

This mechanism is consistent with the measurements of Dabrowski and co-workers,^{24,25} who argued for a mixed $\text{Cr}^{4+}/\text{Cr}^{3+}$ situation based on structural properties and magnetic data, but suggested a minority-spin double-exchange mechanism for the enhanced T_C . It is also consistent with Ru nuclear magnetic resonance (NMR) data of Han and co-workers,²² which showed that the Ru d bands near E_F are broadened upon Cr substitution. It is consistent as well with the reduced effective moment that they found for Cr relative to the ideal value for Cr^{3+} .

Most exchange mechanisms in solids are due to spin-dependent hybridization.^{37,38} The mechanism discussed here

is of this type. It is related to but different from the mechanism proposed for the high value of the Curie temperature in the double perovskite $\text{Sr}_2\text{FeMoO}_6$.³⁹⁻⁴¹ These double perovskites have a strongly hybridized electronic structure with approximately one d electron on the Mo site. Because of hybridization with Fe d^5 local moments, the Mo d orbital also becomes spin polarized, with an antiferromagnetic alignment to the Fe moments. Since the Fe occurs on alternating sites along the Cartesian directions in the double perovskites and this antiferromagnetic Fe-Mo-Fe coupling is strong, a high- T_C ferrimagnetic state is realized. As was discussed by Kanamori and co-workers,^{40,41} this mechanism is closely tied to the double-exchange mechanism of Zener.⁴²⁻⁴⁴ The essential aspect is the spin-dependent hybridization between Fe and Mo (via O) that induces Mo moments and defines their orientation with respect to Fe. Because the moments are induced, Hund's coupling on Mo plays an important role in further stabilizing the ground state and the magnitude of the exchange splitting of the Mo states is determined by the hybridization.

In Cr-doped SrRuO_3 there is also a strong antiferromagnetic coupling between Cr and the SrRuO_3 host (also via O). However, the interaction is between a ferromagnetic host (SrRuO_3) and, as we showed above, well-defined Cr local moments. The magnitude of the exchange splitting of the Cr states is fixed by the local magnetic interaction on Cr, although there are small enhancements of both the Cr and neighboring Ru moments for the ground-state antiferromagnetic alignment. Thus, the mechanism that is operative here is an ordinary antiferromagnetic coupling of a magnetic ion to a ferromagnetic host due to band structure effects. Specifically, with Cr moments antiferromagnetically aligned with the SrRuO_3 , there is better hybridization of Cr and host lattice states spanning the Fermi energy and this leads to an energy lowering in the usual way.

V. SUMMARY AND CONCLUSIONS

Supercell calculations for Cr substitutions in SrRuO_3 show strong spin-dependent hybridization between the majority spin Cr t_{2g} orbitals and O p -Ru t_{2g} -hybridized bands. This hybridization strongly favors antiferromagnetic alignment of the Cr moments with the host lattice magnetization. The energy scale associated with the Cr-host-lattice magnetic interaction is much higher than the magnetic ordering energy of the host lattice on a per transition metal ion basis. This provides an explanation for the large increase in the Curie temperature of SrRuO_3 with Cr substitution.

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