Three-dimensional metallic and two-dimensional insulating behavior in octahedral tantalum dichalcogenides

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Using density functional theory with added on-site interactions, we study the electronic structure of bulk, monolayer, and bilayer of the layered transition-metal dichalcogenide $1T$-TaS_2. We show that a two-dimensional spin-$\frac{1}{2}$ Mott phase exists for the monolayer in the charge density wave (CDW) state and that such a phase is systematically destroyed by packing of the distorted layers leading to a one-dimensional metal for bulk, CDW-distorted TaS_2. The latter finding is in contrast with previous dynamical mean-field theory predictions—we explain the disagreement by the weak effective interaction felt by the electrons in the CDW state. Experimental observations of insulating behavior may arise from disorder due to stacking faults.

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Layered transition metal dichalcogenides (TMDCs) exhibit a wealth of competing phenomena, ranging from charge density waves (CDWs) [1,2] to metal-insulator transitions [2,3] and superconductivity [4]. Recent progress in mechanical exfoliation and device fabrication now allows for electrical characterization and gating of planar samples as thin as one unit cell [5], opening new avenues for the study of basic physics and the integration of TMDC materials into functional components of planar devices. An appealing property of TMDCs with respect to other two-dimensional materials such as graphene is their variable band gap. Some TMDC compounds have optical absorption spectra well matched to the solar spectrum, and in the TMDC material molybdenum disulfide, the passage from bulk material to few-layer compounds has been experimentally shown to impact the magnitude and the nature of the gap [6]. Considering the TMDC family as a whole, the multiplicity of competing energy scales, including interlayer coupling and electron-electron and electron-phonon interactions, suggests a high degree of tunability of the optoelectronic properties, which requires investigation.

Among TMDCs, $1T$-TaS_2 and $1T$-$TaSe_2$ are of particular interest for their interplay of CDW and Mott physics. Below a critical temperature of T_C (180 K for $1T$-TaS_2 [4] and 350 K for $1T$-$TaSe_2$ [7]), the materials exhibit a so-called Star-of-David CDW involving an in-plane, $\sqrt{13}\times\sqrt{13}R = 13.5^\circ$ periodic-lattice distortion (PLD). For $1T$-TaS_2, this PLD coincides with an increase of the resistivity [4] and the appearance of an in-plane gap [7–13]. This behavior has generally been attributed to the opening of a correlation (Mott) gap on the Ta-d_{z^2} subband localized at the star centers in the CDW state [3,10,11,14], although some works have instead attributed it to a transition from a two-dimensional (2D), in-plane metal to 1D, out-of-plane metal with an Anderson-type transition due to packing disorder of the centers of the distortions [8,15–17].

In this paper, we use density functional theory (DFT) and density functional theory with added on-site interactions (DFT + U) methods to contrast single-layer, bilayer, and bulk $1T$-TaS_2 in its CDW state. We find that bulk $1T$-TaS_2 is an out-of-plane metal rather than a Mott insulator, in disagreement with the conventional wisdom [10,11,14] but in agreement with some previous interpretations of experimental data [8,15–17], while the monolayer is a Mott insulator with negligible magnetic exchange interactions and the bilayer compound exhibits a dimer singlet phase. The key to the physics is the Star of David distortion: each unit cell of the distorted structure hosts one orbital at the Fermi level. While the frontier orbital in one cell is localized to the point that hybridization of the frontier orbitals in adjacent cells in the same plane is negligible, the orbital is sufficiently delocalized that (as we show in detail below) the effective Coulomb interaction (U_{eff}) is remarkably weak, and in particular is smaller than the interplane bandwidth (W). The disagreement in the theoretical literature on the nature of bulk $1T$-TaS_2 stems from the parametrization of the U_{eff}/W ratio, rather than from the level of theory used for describing electron-electron interactions. Our work shows how the interplay of dimensionality, correlation strength, and lattice distortion can affect band gaps and magnetic properties in this important class of materials.

The DFT calculations presented here were performed using the Vienna *ab initio* simulation package (VASP) [18–21], with a generalized gradient approximation (GGA) + U [22] approach, a plane-wave basis, and projector-augmented wave (PAW) potentials [23]. We used an energy cutoff of 350 eV, the tetrahedron method with a $14\times14\times8$ k-point mesh with respect to the primitive cell for the computation of the self-consistent electronic densities and the structure relaxations, and a denser, $28\times28\times16$ mesh for the computation of the densities of states. To more accurately represent electronic correlations, an on-site U was included for the tantalum $5d$ orbitals. The value of $U = 2.27$ eV was calculated using a linear-response method [24] for the undistorted bulk. We considered additional values of U in the $\in [0;6]$ eV range, and will discuss their impact in detail below. For all calculations, we relaxed the unit cell in the in-plane direction while keeping the unit cell constant along the c axis. The Star of David (SD) phase of bulk $1T$-TaS_2 was modeled using a $\sqrt{13}\times\sqrt{13}\times2$ unit cell containing 26 tantalum atoms. Monolayers and bilayers were modeled using unit cells with the equivalent of four layers (23.6 Å) of vacuum along the

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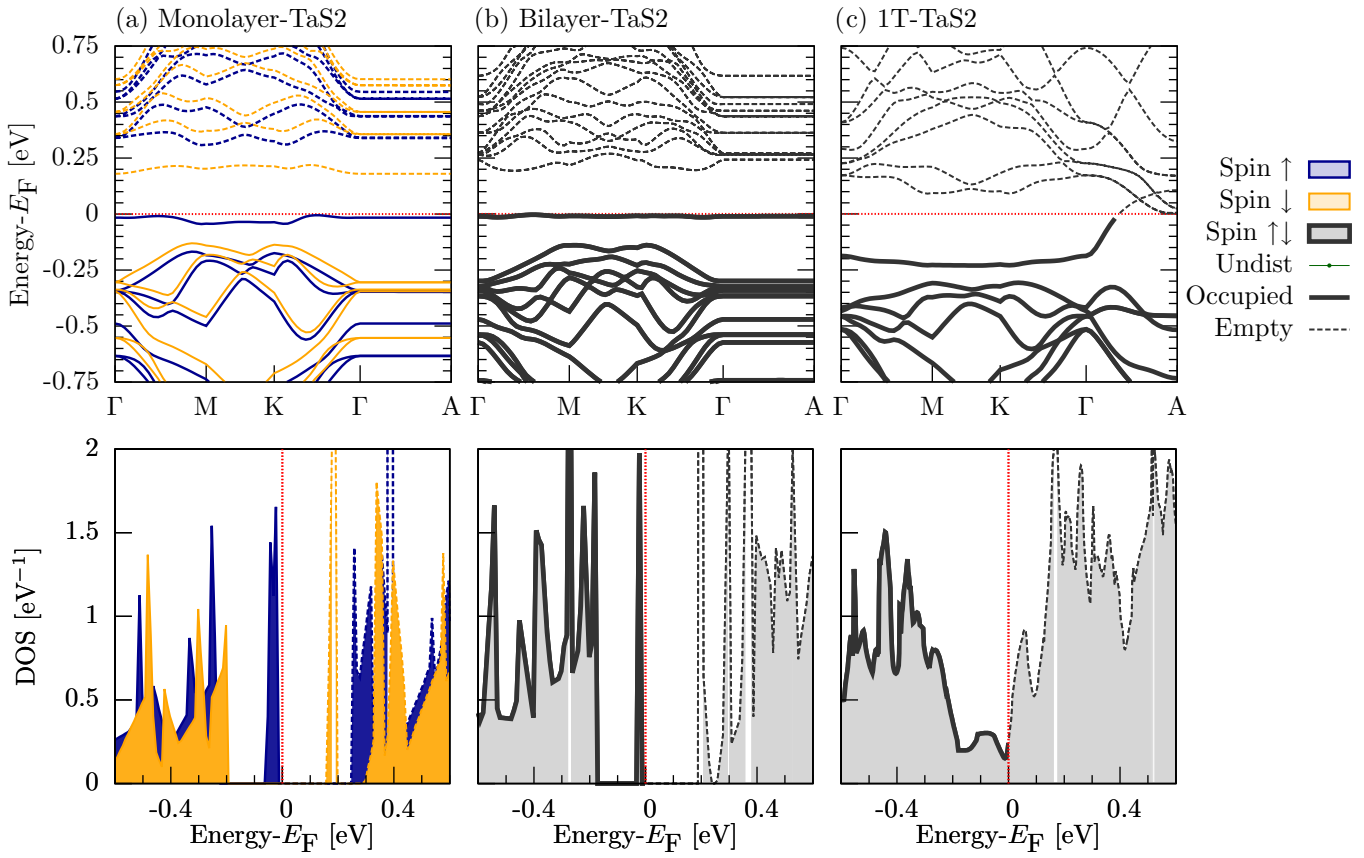

FIG. 1. (Color online) Spin-resolved band structures (top) and density of states (bottom) for the distorted (a) monolayer, (b) bilayer, and (c) bulk of TaS_2 computed with GGA + U ($U = 2.27$ eV) for vertically stacked centers of distortion. The red dotted line indicates the Fermi energy.

c axis to prevent unphysical interactions between periodic images. For all of the systems, the PLD ground states were found by relaxing the atomic positions from a randomized version of their high-symmetry positions in the $\sqrt{13} \times \sqrt{13}$ unit cell.

In agreement with previous studies of bulk $1T$-TaS_2 [25,26] at $U = 0$, the SD structure is found to be more stable than the undistorted structure by 11 meV/TaS_2. The SD structure is found to be more stable than the undistorted structured for all values of the on-site electron-electron interaction and interlayer distance considered in this paper and is also obtained for non-spin-polarized calculations. The energy gain on distortion is almost the same for the spin-polarized and non-spin-polarized calculations (difference <0.1 meV/TaS_2), suggesting that the distortion is not due to correlation effects in the Ta d shell. This small energy difference also suggests that the critical temperature for the magnetic ordering out of plane is very low as both the energy associated with the antiferromagnetic ordering found in DFT and the density of states at the Fermi level are small. As will be shown below, even for T below the Curie-Weiss temperature, bulk $1T - TaS_2$ is a one-dimensional metal with a bandwidth ≈0.45 eV and a small effective U, so we expect the susceptibility will exhibit a Curie-Weiss law with a Weiss temperature much greater than room temperature. Observation of this susceptibility is obscured by the presence of Ta defects, which, as noted by Isa *et al.* [27], produces an additional extrinsic contribution that obscures the susceptibility predicted here. Experiments on monolayers and bilayer may reveal the magnetic behavior predicted here. We find a similar SD structure in the monolayer and bilayer of TaS_2, where the SD distorted structures are found to be 19 and 20 meV/TaS_2 more stable, respectively, than their high-symmetry counterparts.

In Fig. 1, we show the DFT + U-computed band structures and density of states for the relaxed SD-distorted monolayer, bilayer, and bulk TaS_2. We see that the distortion primarily affects the states within approximately ±0.5 eV of the Fermi level, opening a gap of ≈0.35 eV, in agreement with photoemission data [8–11] but leaving a narrow band of states near the Fermi level. The band of in-gap states arises from Ta d_{z^2} orbitals (see Supplemental Material [28]) and has a very weak in-plane (Γ-M-K) dispersion, but in the bulk material disperses very significantly along the interplane direction, with a c-axis bandwidth of ≈0.45 eV and a Fermi-surface crossing between Γ and A. Thus, we conclude that the distorted phase of the bulk $1T$-TaS_2 is a one-dimensional metal, in agreement with previous DFT results for distorted bulk $1T$-TaS_2 [16,29], as well as $1T$-$TaSe_2$ [17,25]. However, previous single-band Hubbard model analyses using U values comparable to the 2.27 eV used here found Mott insulating behavior [10,11,14,29]; we will explain the difference below.

The band structures and density of states presented here are obtained without including spin-orbit coupling. We also present in the Supplemental Material [28] calculations with

spin-orbit coupling. As can be seen, there is a minimal effect on the band structure of distorted bulk $1T$-TaS_2, with a maximal shift of 50 meV (at A). In the undistorted structure, the effect of spin-orbit coupling is larger and manifests itself by a splitting up to 0.2 eV of the d bands at Γ, K, and A, even though the bandwidths in and out of plane are unaffected.

The metallic behavior is solely a consequence of the interplane dispersion: the bilayer and monolayer compounds are insulators. In the DFT + U approximation used here, the monolayer is found to be a ferromagnet with a spin splitting of $\approx$0.18 eV, but the in-plane magnetic coupling is negligible and we interpret the result as indicating that monolayer $1T$-TaS_2 is a Mott insulator with Mott gap $\approx$0.2 eV. The bilayer compound is antiferromagnetic, with opposite spin alignment on the two planes. The out-of-plane antiferromagnetic behavior is an artifact of the DFT + U approximation, which does not treat spin rotation invariance correctly, and we interpret that result as indicating that the spins in the two planes form a singlet state. It is worth noticing that the correlation gap of the monolayer (0.18 eV), which one may identify with the effective U of the Hubbard-like model describing the low-energy physics, is found to be much smaller than the on-site Ta-d calculated value of $U = 2.27$ eV.

To quantify the effect of the interlayer interactions and their competition with the electron-electron interactions, we show in Fig. 2 the magnetic and metal-insulator phase diagram of bulk gap $1T$-TaS_2 as given in GGA + U as a function of the on-site U and interlayer distance c, measured relative to the experimental value $c_{\rm exp} = 5.897$ Å. We consider two choices of interplane stacking of the CDW distortion: a vertical stacking in which the centers of the Stars of David line up from layer to layer and a trigonal stacking (Ta-I upon Ta-III) in which the centers are displaced. At large-c values ($c > 1.3c_{\rm exp}$), the system becomes essentially identical to the monolayer: a Mott insulator with a gap of $\simeq 0.08 \times U$ (eV). For the trigonal stacking (right panel), the system is ferromagnetic for

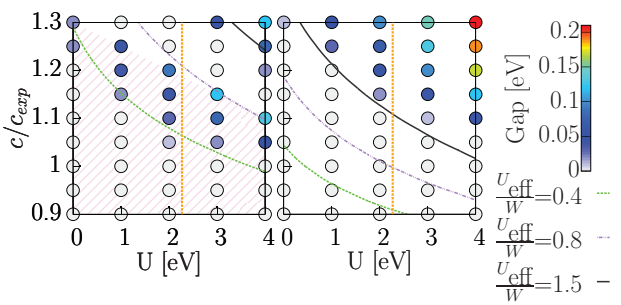

FIG. 2. (Color online) Phase diagram of distorted $1T$-TaS_2 in plane of atomic on-site electron-electron interaction U and interlayer distance c, for vertical (left) and trigonal (right) stackings of the centers of distortion. The contours in the left and right panels indicate the 0.4 (dotted green line), 0.8 (dashed red line), and 1.5 (solid black line) contours of the parametrized $\frac{U_{\rm eff}}{W}$ ratio [$U_{\rm eff}$ is the effective interaction as defined in Eq. (1); W is the out-of-plane bandwidth calculated in DFT for $U = 0$]. Gaps in the insulating state are indicated by colors. In each panel, the vertical orange line indicates the calculated value $U = 2.27$ eV for undistorted bulk $1T$-TaS_2. The hashed and plain areas, respectively, indicate out-of-plane antiferromagnetic and ferromagnetic ground states.

all parameter values considered. An apparently second-order phase transition (solid black line, $U_{\rm eff}/W = 1.5$) separates a Mott insulator from a ferromagnetic metal. For the vertical stacking (left panel), the phase diagram is more complicated, with the large-U, large-c Mott insulator undergoing a transition to a reentrant paramagnetic metal phase (phase boundary approximately coincides with solid black line, $U_{\rm eff}/W = 1.5$) which is separated from the small-U antiferromagnetic metal phase by an intermediate antiferromagnetic insulating phase approximately bounded by the dashed and dotted lines ($U_{\rm eff}/W = 0.8$ and 0.4).

At the theoretically obtained atomic intra-d U value $\approx$2.27 eV (vertical lines), the metal-insulator transition occurs at $c \approx 1.15c_{\rm exp}$ for the trigonal stacking and $c \approx 1.05c_{\rm exp}$ for the vertical stacking. We suggest that pressure (to decrease the lattice constant) and intercalation [30] (to increase it) experiments would be very interesting.

To understand these findings, we present in the top panel of Fig. 3 the spin density of the monolayer system. Because in the DFT + U approximation used here the monolayer is a fully polarized ferromagnet, the spin density is equivalent to the charge density associated with the lower Hubbard band. The spin density is centered around the center of the SD, but with a non-negligible weight on the neighboring tantalum and sulfur atoms, and significant spreading along the out-of-plane direction. The atomic projection of the lower-Hubbard band of the monolayer, obtained by integrating the atom-projected density of states in the range $[E_F - 0.1 : E_F]$ is presented in Fig. 3(b). Though 79% of the lower-Hubbard band lies on the tantalum atoms, only 20 to 25% is localized at the center of the distortion [Ta-I, following the notation in Fig. 3(b), inset], while the other 12 tantalum atoms each have non-negligible projections around 4–6% (these values are found to be weakly dependent on U).

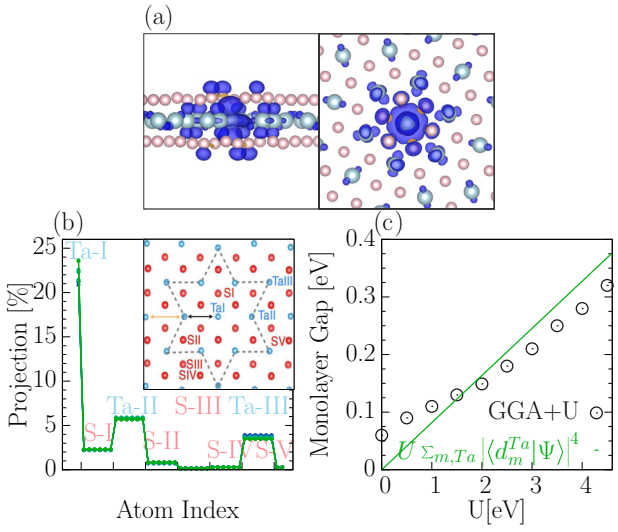

FIG. 3. (Color online) (a) Side and top views of the spin density for monolayer TaS_2. Spin-up (-down) isosurfaces are indicated in blue (orange). (b) Atom-projected integrated charge density in the range $[E_F - 0.1; E_F]$ for different values of the on-site electron-electron interaction U ($U \in$ [0 eV; 4 eV]), for the monolayer of TaS_2. (c) Corresponding effective electron-electron interaction $U_{\rm eff}$ compared with the gap of the monolayer computed in DFT.

This in-plane delocalization is the origin of the weak effective electron-electron interaction (0.18 eV) relevant to the band in the gap. In essence, the small amplitude for the electron to be localized on any given Ta site of the SD implies that the effective interaction U_{eff} is much smaller than the basic on-site Ta interaction U. The difference may be quantified by projecting the Wannier function $|\Psi\rangle$ of the band in the gap onto the local d orbitals, $|d_{am}\rangle$ (here, a labels the Ta sites in one unit cell and m is the angular momentum quantum number), as the effective interaction can be approximated by the Coulomb integral:

$$\frac{U_{\text{eff}}}{U} = \sum_{a\in\star,m} |\langle d_{am}|\Psi\rangle|^4. \quad (1)$$

As seen in Fig. 3(c), evaluation of Eq. (1) leads to an effective interaction that is much smaller (≈8%) than the on-site U, in good agreement with the gaps of the monolayer obtained for GGA + U calculations at different U values (the deviations visible at very small U values arise from the correlations already present in GGA). For the calculated atomic value of $U \approx 2.27$ eV, this effective electron-electron interaction, $U_{\text{eff}} = 0.18$ eV, is larger than the in-plane bandwidth (70 meV), explaining the Mott insulating nature of behavior of the monolayer, but is much weaker than the out-of-plane bandwidth of the bulk (0.45 eV), indicating that the bulk material should not be considered as a Mott insulator. These results suggest that the reported insulating behavior of bulk TaS_2 arises from disorder in a one-dimensional conduction band, as previously proposed [8,15]. In this regard, we remark that the interplane hopping in the trigonally stacked structure is a factor of ≈3 smaller than in the vertically stacked structure, suggesting that the localizing disorder may originate from stacking faults.

The interplay between hopping and interaction leads to interesting results in the bilayer case, where two vertically displaced SD units may be modeled as a two-site Hubbard model, with interaction U_{eff} and hopping t equal to one-quarter of the c-axis bandwidth, i.e., $t \approx 0.1$ eV for the vertically stacked case and $t \approx 0.035$ eV for the trigonally stacked case. Solving the resulting two-site Hubbard model leads to an even-parity singlet ground state, with a triplet excited state about 0.08 eV (vertical) and 0.012 eV (trigonal) higher, and an optical gap (relevant for E fields applied perpendicular to the plane) of 0.25 eV (vertical) or 0.19 eV (trigonal). The sensitivity of the gaps to the interlayer hopping amplitude suggests that optical and magnetic transitions in the bilayer compound may be tuned by intercalation, pressure, and stacking, potentially leading to an interesting set of excitonic transitions.

By approximating the bandwidth W by the bandwidth of the non-spin-polarized distorted bulk at $U = 0$, and U_{eff} as the gap of the monolayer, we find that GGA + U gives the metal-insulator transition for the ferromagnetic ground state at $\frac{U_{\text{eff}}}{W} \simeq 1.5$, in good agreement with the critical value $\frac{U_{\text{eff}}}{W} \simeq 1.3$ for the metal-insulator transition emerging from dynamical mean-field theory (DMFT) calculations [10,14,29]. We therefore suggest that the disagreement between our results and those of Refs. [10,14,29] arises in part from an excessively large value of U assumed in those references. Moreover, the sensitivity of the location of the metal-insulator phase boundary to the nature (ferromagnetic vs antiferromagnetic) of the magnetic state suggests that any insulating states that do occur in the $1T$-TaS_2 family of materials may be regarded as arising more from out-of-plane antiferromagnetic order than from the Mott phenomenon *per se*. Moreover, we observe that the dependence of magnetic ordering on stacking of distortions, as well as the small effective U values, suggests that mappings onto Hubbard models be regarded with caution. The details of the underlying wave functions and of nearby perhaps virtually occupied states, which are not easily represented in a Hubbard model, will be important. Finally, an important challenge raised by our work is understanding the photoinduced dynamics of the out-of-plane metallic bulk $1T$-TaS_2, as the observed collapse of the in-plane gap happens on a time scale that is inconsistent with the dynamics of a Peierls insulator [11].

In conclusion, we have shown that the electronic structure of $1T$-TaS_2 in its CDW state strongly depends on interlayer interactions. In particular, we identify the distorted monolayer of TaS_2 as a Mott insulator, with one localized $S = 1/2$ carrier per 13 atom cluster. Finally, we have revisited the nature of the bulk $1T$-TaS_2, which we predict to be a band insulator in plane and metallic out of plane upon distortion, and explained the disagreement with previous interpretations by the weak effective electron-electron interactions felt by the electrons delocalized across the SD. The monolayer compounds are predicted to be Mott insulators with a $S = 1/2$ degree of freedom in each unit cell of the CDW structure, while the bilayers form a singlet state with a tunable optical gap.

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[1] J. A. Wilson, F. J. Di Salvo, and S. Mahajan, *Advances in Physics* (Taylor & Francis, London, 1975).
[2] J. A. Wilson and A. D. Yoffe, Adv. Phys. **18**, 193 (1969).
[3] P. Fazekas and E. Tosatti, Philos. Mag. Part B **39**, 229 (1979); Physica B + C **99**, 183 (1980).
[4] B. Sipos, A. F. Kusmartseva, A. Akrap, H. Berger, L. Forró, and E. Tutiš, Nat. Mater. **7**, 960 (2008).
[5] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl. Acad. Sci. USA **102**, 10451 (2005).

[6] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **105**, 136805 (2010).
[7] S. Colonna, F. Ronci, A. Cricenti, L. Perfetti, H. Berger, and M. Grioni, Phys. Rev. Lett. **94**, 036405 (2005).
[8] B. Dardel, M. Grioni, D. Malterre, P. Weibel, Y. Baer, and F. Lévy, Phys. Rev. B **45**, 1462(R) (1992).
[9] S. Hellmann, M. Beye, C. Sohrt, T. Rohwer, F. Sorgenfrei, H. Redlin, M. Kalläne, M. Marczynski-Bühlow, F. Hennies, M. Bauer, A. Föhlisch, L. Kipp, W. Wurth, and K. Rossnagel, Phys. Rev. Lett. **105**, 187401 (2010).
[10] L. Perfetti, A. Georges, S. Florens, S. Biermann, S. Mitrovic, H. Berger, Y. Tomm, H. Höchst, and M. Grioni, Phys. Rev. Lett. **90**, 166401 (2003).
[11] L. Perfetti, P. A. Loukakos, M. Lisowski, U. Bovensiepen, H. Berger, S. Biermann, P. S. Cornaglia, A. Georges, and M. Wolf, Phys. Rev. Lett. **97**, 067402 (2006).
[12] J.-J. Kim, W. Yamaguchi, T. Hasegawa, and K. Kitazawa, Phys. Rev. Lett. **73**, 2103 (1994).
[13] D. Stoltz, M. Bielmann, M. Bovet, L. Schlapbach, and H. Berger, Phys. Rev. B **76**, 073410 (2007).
[14] L. Perfetti, P. A. Loukakos, M. Lisowski, U. Bovensiepen, M. Wolf, H. Berger, S. Biermann, and A. Georges, New J. Phys. **10**, 053019 (2008).
[15] F. J. Di Salvo and J. E. Graebner, Solid State Commun. **23**, 825 (1977).
[16] M. Bovet, S. van Smaalen, H. Berger, R. Gaal, L. Forró, L. Schlapbach, and P. Aebi, Phys. Rev. B **67**, 125105 (2003).
[17] M.-T. Suzuki and H. Harima, J. Magn. Magn. Mater. **272–276**, E653 (2004).
[18] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[19] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
[20] G. Kresse and J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996).
[21] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
[22] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).
[23] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[24] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).
[25] Y. Ge and A. Y. Liu, Phys. Rev. B **82**, 155133 (2010).
[26] A. Y. Liu, Phys. Rev. B **79**, 220515 (2009).
[27] T. Isa, T. Fukase, M. Sasaki, M. Koyano, N. Taniguchi, T. Kimura, Y. Isobe, and H. Negishi, J. Low Temp. Phys. **127**, 63 (2002).
[28] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.90.045134 for more information on the relaxed atomic structures, the spin-orbit-corrected band structures, the wavefunctions, and the magnetism of the compounds discussed in this article.
[29] J. K. Freericks, H. R. Krishnamurthy, Y. Ge, A. Y. Liu, and T. Pruschke, Phys. Status Solidi B **246**, 948 (2009).
[30] H. I. Starnberg, Mod. Phys. Lett. B **14**, 455 (2000).