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Formation of an unconventional Ag valence state in Ag_2NiO_2

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The Ag ion in the recently synthesized novel material Ag_2NiO_2 adopts an extremely unusual valency of $\frac{1}{2}$, leaving the Ni ion as 3+, rather than the expected 2+. Using first-principles calculations, we show that this mysterious subvalent state emerges due to a strong bonding-antibonding interaction between the two Ag layers that drives the lower band beneath the O p complex, eliminating the possibility of a conventional Ag 1+ valence state. The strong renormalization of the specific heat coefficient γ is likely due to strong spin fluctuations that stem from nearly complete compensation of the ferromagnetic (metallic double exchange and 90° superexchange) and antiferromagnetic (conventional superexchange via Ni-O-Ag-O-Ni path) interactions.

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As with other noble metals, Ag typically adopts a formal valence of 1, 2, or 3 in a compound, corresponding to an empty s shell and either a full or partially depleted d shell. Any valence less than 1 would leave the Ag s shell partially filled and is therefore rather unnatural, particularly with strong oxidizers such as O or F. One noted case in which Ag assumes a formal valency of $\frac{1}{2}$ is Ag_2F,[1,2] and this compound is rather unstable, decomposing in the presence of water, ultraviolet light, or above 80 °C.

Since F^{2-} cannot exist in nature, Ag in Ag_2F is perforce $\frac{1}{2}$+. On the other hand, Ni^{2+} is a common oxidation state for nickel, just as Ag^+ is for silver, and one would therefore anticipate that the Ag_2NiO_2 compound should form, with Ag^+ and Ni^{2+} oxidation states, and thus be a magnetic insulator, like NiO. Recently Ag_2NiO_2 has been synthesized[3] and, intriguingly, did not fit this picture.[3,4] It remained metallic down to the lowest measured temperatures, with properties rather close to those of delafossite $AgNiO_2$, a nearly isostructural compound with one fewer silver atom.[5] This has been interpreted as a signal that Ag is underoxidized, or subvalent $[Ag_2]^+$, leaving Ni in a 3+ state.[3] In such a case it would indeed be similar to $AgNiO_2$ as well as to the better known nickelates $LiNiO_2$ or $NaNiO_2$, with the low-spin ($t_{2g}^6e_g^1$) Ni^{3+} being a Jahn-Teller (JT) ion. Not surprisingly then, just as in $NaNiO_2$, a structural transition from a high-temperature rhombohedral phase to a (presumably) monoclinic phase was reported in Ag_2NiO_2 at $T_s=260$ K.[3,4,7] This was attributed in Ref. 4 to a cooperative Jahn-Teller transition of Ni^{3+}, accompanied by orbital ordering (OO), although this attribution was later questioned.[6]

This compound poses one principal puzzle: why does Ag assume such an unnatural valence state instead of the expected combination of Ag^+ and Ni^{2+}? Additionally, there are unexplained phenomena such as the large electronic specific heat coefficient $\gamma=19$ mJ/mol K (Ref. 24) and the undetermined nature of the magnetic ordering. The layered nickelates and cobaltates, if magnetic, usually show an A-type antiferromagnetism (AFM) setting in at low temperature. Ag_2NiO_2 has a Néel temperature of 56 K,[3] but the ordering type is unknown, and there are speculations[6] that it is not A-type, but rather AFM in-plane and possibly incommensurate. Unlike most similar materials, the Curie-Weiss temperature changes sign at the structural transition $T_s=260$ K,[3] with the high-temperature undistorted phase showing net FM spin fluctuations ($\Theta=10$ K) and the low-temperature phase exhibiting AFM ones ($\Theta=-30$ K), both lower than the observed ordering temperature ($|\Theta|<T_N$).

Using first-principles calculations we demonstrate that most, if not all, of these puzzles can be resolved at the one-electron level. The half-valent silver in this compound appears due to strong bonding-antibonding splitting in the Ag bilayer that pushes most of the bonding Ag s band below the Ni d complex and below most of the O p states. The magnetic disparity with the other layered nickelates and cobaltates can be explained by the fact that hopping between orthogonal O p orbitals on the same site becomes possible via the metallic Ag layers, thus creating a path for an AFM exchange that compensates the usual metallic FM double exchange and the 90° FM superexchange via oxygen. This compensation leads to strong spin fluctuations that may be responsible for the large specific heat.

The high-temperature crystal structure of Ag_2NiO_2 is rhombohedral ($R\bar{3}m$), consisting of close-packed triangular layers of O-Ni-O-Ag-Ag-O-Ni-O, with edge-sharing NiO_6 octahedra. The stacking sequence is $ABCABC$ so that the Ni layers form a $BACBAC$ sequence. For this phase, we used the structural parameters from Ref. 3. We also performed calculations in the monoclinic ($C2/m$) structure suggested by Jansen.[7] We used a full-potential augmented plane-wave with local orbitals (APW+lo) method.[9] To ensure complete convergence we used up to 1024 inequivalent k points with $RK_{\max}=7$. For magnetic supercell calculations, described in detail later, we used up to 140 k points in the (now 4 times smaller) Brillouin zone and $RK_{\max}$ up to 9. Gradient corrections to the exchange correlation potential were included in form of Ref. 10. The calculated band structure appears to correspond to the $Ag^{0.5+}$-Ni^{3+} combination, as conjectured by Schreyer and Jansen.[3] To understand the microscopic reasons for this unusual result, we employed an orbital downfolding procedure as built into the linear muffin-tin orbital (LMTO) method in the atomic spheres approximation (ASA).[8]

We begin by investigating the high-temperature structure,

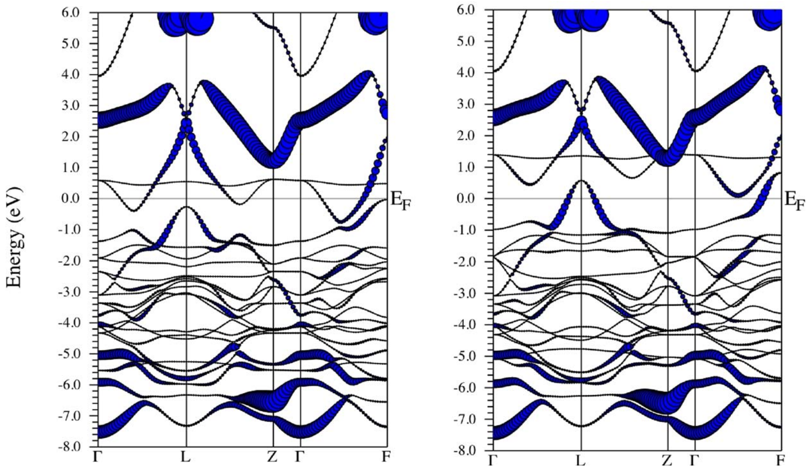

FIG. 1. (Color online) LAPW band structure obtained with the generalized gradient approximation (GGA) for majority (left panel) and minority (right panel) spins. Ag *s* character is indicated by the size of the dark (blue) circles.

assuming FM ordering. The local augmented plane-wave (LAPW) bands with the Ag *s* character emphasized are shown in Fig. 1. One can see a nearly free electron band that starts at ∼−8 eV at the Γ point, gets lost in the manifold of the O *p* and Ag *d* bands between ∼−7 and ∼−2 eV, and reappears above the Fermi level at *L* and *F*. Surprisingly, the bottom of this band (at Γ) lies *below* the bottom of the O *p* bands (at *L*). This band originates from the Ag *s* and *p* states, and since it starts below the O *p* states, the valence of Ag, no matter how one chooses to define it, must be less than 1. A more specific evaluation of the Ag valency is difficult, but an estimate can be made by counting the electrons contained in the Ag-derived Fermi surface (FS). We find 0.47 electrons, extremely close to the expected value of 0.5, though such agreement is largely fortuitous since band hybridization obscures the true electron count. The Ni *d* bands are narrower and less hybridized, making the concept of Ni valency more defined and easier to establish. The Ni *d*-band occupancy corresponds to a Ni^{3+} state, consistent with the measured μ_{eff} both above and below the structural transition.[4] This again points to $\mathrm{Ag}^{1/2+}$ as the correct valency.

The obvious question is, how can the conductivity band of an *s* metal drop below O *p* states? To answer this question, we separate the band structure into individual contributions, using the band-downfolding technique of the LMTO method. Figure 2(a) shows the LMTO bands in the same structure, but, for simplicity, without spin polarization. We observe that the qualitative character of the LAPW bands, including the relative positions of the Ag and O bands, is reproduced. We first remove from the LMTO basis set all states except Ni 3*d* and O 2*p*. Note that the self-consistent potential for the real compound is still used, so the resulting band structure is *not* the same as for a hypothetical $\mathrm{NiO_2}$ with the Ag atom removed. It represents the actual Ni and O states in $\mathrm{Ag_2NiO_2}$, but without hybridization with other bands. The bottom of the O 2*p* at bands at ∼−5 eV is shifted away from the Γ point, and the top overlaps the Ni 3*d* band around −2 eV. We can also remove Ni 3*d* and O 2*p* from the basis, leaving only Ag *s*, *p*, and *d*. In this case, we clearly see two bonding and antibonding *sp* bands that are free-electron-like along in-plane directions (emphasized in Fig. 2 in green). The bonding band intersects the narrow Ag *d* bands and finally reappears below the lowest O *p* band. The bonding-antibonding splitting is very large, encompassing half the full band dispersion from the Γ point to the edge of the Brillouin zone, due to the six nearest-neighbor in-plane Ag ions, compared to three adjacent plane neighbors.

The bonding-antibonding splitting is the principal feature that distinguishes $\mathrm{Ag_2NiO_2}$ from the similar one-Ag-layer delafossite $\mathrm{AgNiO_2}$. The latter behaves more like other $A\mathrm{NiO_2}$-based layered materials (A=alkaline), such as $\mathrm{LiNiO_2}$ or $\mathrm{NaNiO_2}$. However, even in the delafossite compound, the Ag *s* band is considerably lower than the alkaline *s* bands, such that the very bottom of the *s* band drops well below the Fermi level (assuring metallicity), but not below the bottom of the O bands. Obviously, it is the bilayer band splitting in $\mathrm{Ag_2NiO_2}$ that pushes the bonding Ag band down compared to $\mathrm{AgNiO_2}$, thus preventing full charge transfer from this band to O. Note that in both silver nickelates the bonding Ag band crosses the Fermi level and spans the same energy range as the bands of the $\mathrm{NiO_2}$ complex, preventing formation of an insulator even after JT splitting.

The combination of heavy *d* and light *sp* electrons in $\mathrm{Ag_2NiO_2}$ should provide interesting transport properties. The FS is comprised of a predominantly Ag *sp* cylinder (Fig. 3, right side) with faster electrons in the spin-minority channel

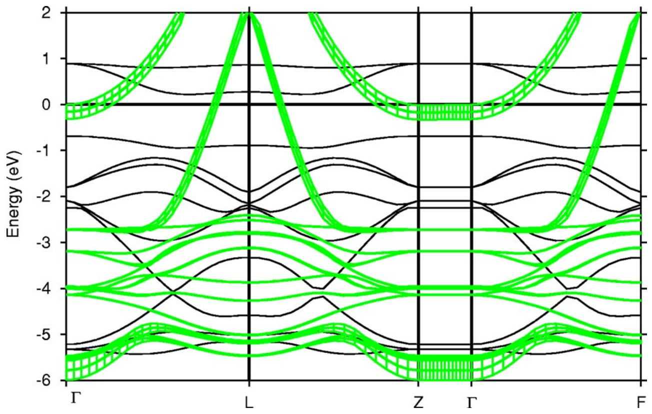

FIG. 2. (Color online) Downfolded LMTO band structure obtained within the local density approximation (LDA): NiO, solid black; Ag, thick gray (green) bands. The amount of Ag s,p contributions is proportional to the broadening (hatched lines) of Ag bands.

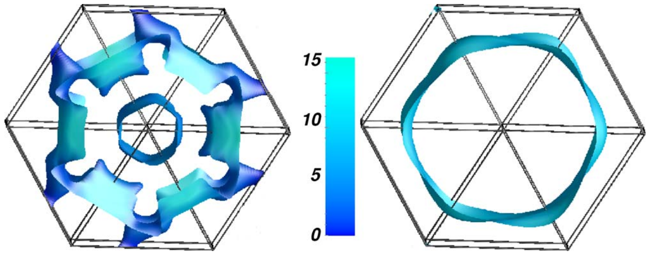

FIG. 3. (Color online) The Fermi surface of Ag_2NiO_2 in the high-temperature (rhombohedral) phase in the spin-majority (left) and spin-minority (right) channels. The minority surface contains fast electrons derived from Ag *s* and *p* bands, while the majority surface contains both slow electrons (central cylinder and outside edge of hexagonal network) and fast electrons (inside edge of network).

(where Ag_2NiO_2 is a two-dimensional free electron metal) and a central hexagonal cylinder with a surrounding network in the spin majority channel, formed by hybridized Ni *d* and Ag *sp* states. The characteristics of the FS in the rhombohedral and monoclinic (to be discussed later) structures are displayed in Table I. Note that the density of states (DOS) is provided mostly by the Ni bands while conductivity is carried by the Ag bands. Though large, the DOS is a factor of 3 short of the experimental number (as estimated from the linear specific heat) in the rhombohedral cell and lessens by another a factor of 2 in the monoclinic cell. One cannot expect an electron-phonon renormalization of this strength, and therefore it must be of electronic origin.

Generally, there are two effects of electronic correlation on the band structure.[11] The first is due to the formation of lower and upper Hubbard bands and is often incorporated in a mean-field way in a method such as LDA+U.[12] However this method works well only for strongly localized electrons, deep on the insulating side of the Mott transition. For situations that are intermediate between localized and itinerant, especially approaching the Mott transition from the metallic side, the LDA+U method incorrectly leads only to a decrease of the DOS at E_F $[N(E_F)]$ and never an enhancement, which may worsen agreement with experiment.[13] We indeed observed this when we carried out LDA+U calculations (in the somewhat simpler LMTO-ASA scheme). Nevertheless, the role of electron correlations in increasing the effective mass cannot be excluded. The second manifestation of correlation is the effective narrowing of the quasiparticle peak near E_F due to dressing by low-lying bosonic excitations, such as soft spin fluctuations. This effect enhances γ and, in general, depresses the magnetic moment. We shall argue that soft spin fluctuations are indeed operative in Ag_2NiO_2.

TABLE I. The plasma frequencies and density of states at E_F for the high-temperature rhombohedral (R) and low-temperature monoclinic (M) structures of Ag_2NiO_2 in the FM configuration.

	ωp_x (eV)	ωp_z (eV)	$N(E_F)$ $(\mathrm{eV})^{-1}$
R (up)	2.83	2.58	2.24
R (dn)	2.96	1.12	0.25
M (up)	3.05	2.67	1.32
M (dn)	3.12	3.06	0.27

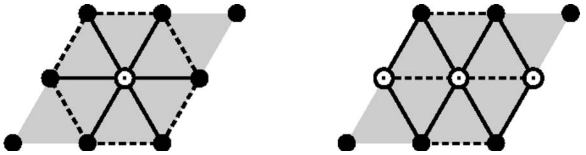

FIG. 4. One supercell of the $\mathcal{FI}$ and $\mathcal{AF}$ in-plane magnetic configurations investigated in this work. Open (solid) circles show-spin up (-down) sites. The 12 unique bonds (FM and AFM) in each supercell are shown.

The typical magnetic configuration for triangular oxide layers with localized electrons is A-type antiferromagnetism, or ferromagnetically aligned planes stacked antiferromagnetically along the (111) rhombohedral direction. The first surprise is that, contrary to the alkali nickelates, the calculated interplane coupling is ferromagnetic (albeit by only 6 meV/Ni), but becomes effectively degenerate (within 0.2 meV/Ni) upon the monoclinic JT distortion. This can be attributed to competition between the AFM interplane superexchange and metallic FM double exchange. The distortion improves the superexchange paths and slightly suppresses the FM double exchange through loss of DOS at E_F.

It has been argued[6] that the in-plane magnetism is itinerant (this could explain why the Curie-Weiss temperature is small compared to T_N) and not FM (possibly incommensurate). To test this computationally, we considered a $2\times 2\times 1$ supercell (Fig. 4). Using a lowered symmetry to allow for three inequivalent Ni sites in the monoclinic (cooperative JT) cell, we created three magnetic patterns $\mathcal{FM}$, $\mathcal{FI}$, and $\mathcal{AF}$. In the $\mathcal{FI}$ pattern half the bonds are AFM and half FM, and three out of four spins are parallel. In the $\mathcal{AF}$ pattern there are two up and two down spins, with 8 AFM and 4 FM bonds. In the nearest-neighbor approximation, $E_{\mathcal{AF}}-E_{\mathcal{FI}}=2J$, where J is the cost of changing one bond from FM to AFM, and $E_{\mathcal{FI}}-E_{\mathcal{FM}}=6J$. Our calculations give $E_{\mathcal{AF}}-E_{\mathcal{FI}}=4.1$ meV and $E_{\mathcal{FI}}-E_{\mathcal{FM}}=15.0$ meV, consistent with a FM $J=2.3\pm 0.2$ meV. Note, however, that this number is very small compared to typical triangular-layer nickelates and cobaltates. Moreover, in the rhombohedral structure $E_{\mathcal{FI}}-E_{\mathcal{FM}}$ is reduced to less than 3 meV, a full compensation (within computational accuracy) of FM and AFM in-plane interactions that can be traced to the effect of silver. The in-plane ferromagnetism is due to 90° superexchange (and to FM double exchange in the metallic bands) since according to the Goodenough-Kanamori-Anderson rule for 90° Me-O-Me bonds the superexchange via orthogonal $2p$ orbitals is ferromagnetic. Indeed, the Ni-O-Ni bond angle in Ag_2NiO_2 is close to 90°, but the metallic Ag bands provide a channel for assisted hopping from one O orbital to another, creating an AFM superexchange path:[14] Ni-O-Ag-O-Ni [a similar mechanism was suggested for $CuGeO_2$ (Ref. 15)]. Competition between the two types of superexchange results in a near compensation for the in-plane exchange, with the net sign depending on details beyond this model. Additionally, the large Ag-derived FS provides for RKKY screening that induces long-range magnetic interactions with alternating signs.

It is clear from the near cancellation of the FM and AFM interaction both in and out of plane that Ag_2NiO_2 is a perfect breeding ground for strong spin fluctuations. The ultimate ordering pattern, then, will depend on fine details of the low-temperature structure. One of the main unanswered questions is whether this structure is JT distorted[7] or not.[6] To address this question computationally we have performed a full structural optimization using a pseudopotential code.[16,17] Optimization in LDA, GGA, or LDA+U invariably gave the high-symmetry rhombohedral structure as the ground state. We have verified this result by calculating total energies for the reported rhombohedral and monoclinic structures[7] in LAPW and again found the former to be lower in energy by 13 meV. While the energy differences involved are too small to definitively eliminate a JT-distorted ground state, our first-principles calculations disfavor it, lending support to the conclusion of Sugiyama *et al.*[6] In light of the already substantial disagreement between calculated and measured $N(E_F)$, the loss of nearly half the DOS upon monoclinic distortion also casts doubt on the JT nature of the low temperature phase.

To summarize, we report all-electron, full-potential first-principles calculations of the electronic, transport, magnetic, and structural properties of Ag_2NiO_2. We confirm earlier conjectures[3] that the valence state of nickel in this compound is practically Ni^{3+}, while the valence of Ag is very close to $\frac{1}{2}$. The microscopic reason for this unusual configuration appears to be the strong bonding-antibonding splitting of the Ag_2 bilayer, which pushes the bottom of the Ag *sp* band below the O *p* bands, resulting in the rather unexpected 3+ Ni valence (because of high covalency in spectroscopic measurements, this should correspond not to a d^7, but rather to a d^8L ground state, where L is a ligand hole). The Ag bilayer also nontrivially affects the magnetic properties, providing an additional FM interaction between the planes, offsetting the standard AFM superexchange, while overlap between the O *p* orbitals and the metallic silver layer effectively removes the orthogonality of the O orbitals and revives an AFM superexchange. The FM and AFM near compensation creates strongly fluctuating spins that may be responsible for the mass renormalization $m^*/m_{band} \approx 3$. Finally, our first-principles calculations cannot reproduce the proposed[7] JT distortion, lending some support to the authors[6] who question this suggestion. Overall, the physics of Ag_2NiO_2 appears to be unexpectedly rich and worth more detailed experimental and theoretical study.

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