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Disentangling orbital and spin exchange interactions for \( \text{Co}^{2+} \) on a rocksalt lattice


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Neutron spectroscopy was applied to study the magnetic interactions of orbitally degenerate \( \text{Co}^{2+} \) on a host MgO rocksalt lattice where no long-range spin or orbital order exists. The paramagnetic nature of the substituted monoxide \( \text{Co}_{0.03}\text{Mg}_{0.97}\text{O} \) allows for the disentanglement of spin exchange and spin-orbit interactions. By considering the prevalent excitations from \( \text{Co}^{2+} \) spin pairs, we extract seven exchange constants out to the fourth coordination shell. An antiferromagnetic next-nearest-neighbor 180° exchange interaction is dominant; however, dual ferromagnetic and antiferromagnetic interactions are observed for pairings with other pathways. These interactions can be understood in terms of a combination of orbital degeneracy in the \( t_{2g} \) channel and the Goodenough-Kanamori-Anderson rules. Our work suggest that such a hierarchy of exchange interactions exists in transition-metal-based oxides with a \( t_{2g} \) orbital degeneracy.

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I. INTRODUCTION

The combination of magnetic exchange and orbital degeneracy has provided the basis for a number of topics in condensed-matter physics including metal-insulator transitions, high-temperature superconductors, colossal magnetoresistance [1–3], and, more recently, Kitaev interactions [4–6]. Rocksalt temperature superconductors, colossal magnetoresistance including metal-insulator transitions, high-temperature superconductors, colossal magnetoresistance have provided the basis for a number of topics in condensed-matter physics.

\( \text{CoO} \) was the first orbitally degenerate compound to have its magnetic structure investigated using neutron diffraction [7–10], but the underlying exchange interactions are still not known. Indeed, calculations and experiment have been performed (for example, in \( \text{KCuF}_3 \) [11]), the case of exchange interactions are a direct result of the underlying exchange interactions with comparable magnitudes. The dual interactions and observe dual ferro- and antiferromagnetic interactions.

The starting point for understanding the spin-orbit Hamiltonian for paramagnetic \( \text{Co}^{2+} \) ions is crystal-field theory based on octahedral coordination [13,14] [Fig. 1(a) for rocksalt CoO] [15–17]. As schematically shown in Fig. 1(b), the octahedral crystal field (\( \hat{H}_\text{CF} \)) splits the five degenerate \( d \) orbitals (\( 4f \)) such that the \( d^7 \) electronic structure consists of five electrons occupying the lower-energy \( t_{2g} \) states and two electrons in the higher-energy \( e_g \) orbitals. This constitutes two orbital triplets (\( 4T_1 \)) levels separated by 10Dq \( \sim 900 \text{ meV} \) [17]. The triplet degenerate \( 4T_1 \) ground state can be approximated to have an effective orbital angular momentum of \( \ell = 1 \) [16–24]. Applying spin-orbit coupling (defined by \( \hat{H}_\text{SO} = \hat{\lambda}_\text{S} \cdot \hat{S} \), with \( \hat{S} = \frac{1}{2} \)) to this orbital ground state results in three effective spin-orbit manifolds classified by an effective angular momentum of \( j_{\text{eff}} = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \) (with \( j_{\text{eff}} = \ell + \frac{1}{2} \)). The \( j_{\text{eff}} = \frac{1}{2} \) ground state is separated from the higher-energy \( j_{\text{eff}} = \frac{3}{2} \) states by \( \frac{3}{2} \lambda \sim 36 \text{ meV} \) [17].

In the presence of long-range magnetic order (as exists in \( \text{CoO} \) at low temperatures), the total single-ion Hamiltonian for \( \text{Co}^{2+} \) can then be summarized by

\[
\hat{H}_\text{SI} = \hat{H}_\text{CF} + \hat{H}_\text{SO} + \hat{H}_\text{MF},
\]

where \( \hat{H}_\text{CF} \), \( \hat{H}_\text{SO} \), and \( \hat{H}_\text{MF} \) are the octahedral crystal-field, spin-orbit, and magnetic-order-induced molecular field. The effect of magnetic ordering on the three-spin-orbit manifolds discussed above can be illustrated by considering a single dominant next-nearest-neighbor 180° \( \text{Co}^{2+} - \text{O}^{2-} - \text{Co}^{2+} \) superexchange \( J_z \) with

\[
\hat{H}_\text{MF} = 2J_z z_2 \hat{S}_z \hat{S}_z,
\]

where \( \hat{S}_z \) is the total magnetic moment parallel to the crystal field. The superexchange interaction is dominant in rocksalt temperature superconductors.

\( \text{Co}^{2+} \) ions have an effective orbital angular momentum of \( \ell = 1 \) and an effective spin angular momentum of \( j = 3/2 \). The magnetic exchange and orbital degeneracy interactions are a direct result of the underlying exchange interactions with comparable magnitudes. The dual interactions and observe dual ferro- and antiferromagnetic interactions.

The octahedral crystal field (\( \hat{H}_\text{CF} \)) splits the five degenerate \( d \) orbitals (\( 4f \)) such that the \( d^7 \) electronic structure consists of five electrons occupying the lower-energy \( t_{2g} \) states and two electrons in the higher-energy \( e_g \) orbitals. This constitutes two orbital triplets (\( 4T_1 \)) levels separated by 10Dq \( \sim 900 \text{ meV} \) [17]. The triplet degenerate \( 4T_1 \) ground state can be approximated to have an effective orbital angular momentum of \( \ell = 1 \) [16–24]. Applying spin-orbit coupling (defined by \( \hat{H}_\text{SO} = \hat{\lambda}_\text{S} \cdot \hat{S} \), with \( \hat{S} = \frac{1}{2} \)) to this orbital ground state results in three effective spin-orbit manifolds classified by an effective angular momentum of \( j_{\text{eff}} = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \) (with \( j_{\text{eff}} = \ell + \frac{1}{2} \)). The \( j_{\text{eff}} = \frac{1}{2} \) ground state is separated from the higher-energy \( j_{\text{eff}} = \frac{3}{2} \) states by \( \frac{3}{2} \lambda \sim 36 \text{ meV} \) [17].

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considering excitations from the dominant Co\textsuperscript{2+} pair response. This paper is divided into four sections, including this introduction. In Sec. II, we first describe the experimental methods including materials preparation and characterization techniques, where we conclude that our dilute sample can be described by a Co\textsuperscript{2+} pair response. An expanded description of the characterization is given in the Supplemental Material [36], illustrating the x-ray, susceptibility, and energy dispersive x-rays (EDX) data [36]. In Sec. III, the theory required to extract both the exchange constant and the distance associated with the interaction is outlined. We then show the experimental data used to derive the exchange interactions. We finally conclude with a discussion of the results, including a comparison with thermodynamic data from pure CoO, and also how we can understand the results in terms of the Goodenough-Kanamori-Anderson (GKA) rules.

II. EXPERIMENTAL DETAILS AND MATERIALS CHARACTERIZATION

To extract individual $J$ constants for Co\textsuperscript{2+}, we have followed the pioneering work on dilute Mn\textsuperscript{2+} [37,38] and Co\textsuperscript{2+} [22] compounds and measured the dilute monoxide Co\textsubscript{0.03}Mg\textsubscript{0.97}O using inelastic neutron spectroscopy. The high magnetic dilution removes the problematic molecular field discussed above [Fig. 1(c)] and suppresses the mixing between $j$ manifolds, allowing us to consider a dominant response for Co\textsuperscript{2+} pairs. Probabilistic arguments can be used to illustrate this and are based on the observation that for a given random distribution of $x$Co\textsuperscript{2+} and $(1-x)$Mg\textsuperscript{2+} ions, the number of Co\textsuperscript{2+} pairs and the number of pairwise interactions for a given geometry present in the lattice far outweighs the number of Co\textsuperscript{2+} triplets and corresponding interactions between three Co\textsuperscript{2+} cations. For example, if there are $N$ ways that a cluster with a particular geometry of three sites $XYZ$ can occur in a given crystal, the relative probabilities of an arrangement of 3 Mg\textsuperscript{2+}, 1 Co\textsuperscript{2+}, and 2 Mg\textsuperscript{2+} (and its permutations), 2 Co\textsuperscript{2+} and 1 Mg\textsuperscript{2+} (and its permutations), and 3 Co\textsuperscript{2+} occupying the three sites $XYZ$ are $(1-x)^3$, $x(1-x)^2$, $x^2(1-x)$, and $x^3$, respectively. Hence the ratio of numbers of spin pairs with $XY$, $XZ$, and $YZ$ geometry to spin triplets with $XYZ$ geometry in the lattice is $\frac{1}{x}$, and thus for small $x$, the number and hence inelastic neutron-scattering intensities of Co\textsuperscript{2+} pair excitations far outweigh those from larger Co\textsuperscript{2+} clusters. We summarize the sample preparation and characterization techniques confirming the dominant pair response in this section, and an expanded description, including data from the techniques, of the characterization is provided in the Supplemental Material [36]. We also discuss the neutron experiments applied to these materials.

Materials preparation. Two polycrystalline samples of Co\textsubscript{0.03}Mg\textsubscript{0.97}O were synthesized for this particular investigation. The first was synthesized by traditional solid-state methods as outlined by Cowley et al. [17]. A second sample of Co\textsubscript{0.03}Mg\textsubscript{0.97}O was made using solution techniques by mixing stoichiometric amounts of Mg(NO\textsubscript{3})\textsubscript{2} $\times$ 6H\textsubscript{2}O and Co(NO\textsubscript{3})\textsubscript{2} $\times$ 6H\textsubscript{2}O. The solid mixture was dissolved in CH\textsubscript{3}CH\textsubscript{2}OH and stirred for 1 h and heated to 70°C for 12 h, yielding a pink gel. The gel was heated in air to 600°C with
a heating rate of 20 °C/h, reacted for 24 h, subsequently heated to 1000 °C with a heating rate of 150 °C/h, held for an additional 48 h, and finally cooled to room temperature by switching off the furnace. Details concerning the synthesis and treatment of MgO and CoO samples are outlined by Cowley et al. [17]. We note that both magnetically substituted MgO samples gave consistent results and the comparison is shown in the Supplemental Material [36].

**Laboratory x-ray diffraction.** Room-temperature powder-diffraction patterns of the end members (CoO and MgO) and Co_{0.03}Mg_{0.97}O synthesized by sol-gel were collected over 2θ = [25,100]° in 0.02° steps on a Bruker D2 Phaser laboratory x-ray diffractometer utilizing a monochromated Cu Kα,1.2 source. As illustrated in the Supplemental Material [36], Rietveld refinement of Mg_{1−x}CoO indicates that the solid solution assumes a rocksalt structure (Fm3m) with a unit-cell parameter a = 4.2131(2) Å. Utilizing the measured values of the end members CoO (4.2594(4) Å) and MgO (4.2118(1) Å), the unit-cell parameter of 4.2131(2) Å corresponds to an x = 0.025(5) according to Vegard’s law [39], supporting that approximately 3% of the Mg²⁺ sites contain Co²⁺.

**Energy-dispersive x-ray analysis.** As a final direct confirmation of the concentration of Co²⁺ in our sample, we performed energy-dispersive x-ray measurements. Elemental analysis was performed using scanning electron microscopy (SEM) on a Hitachi SU-70 Schottky field-emission gun SEM with Energy-dispersive x-ray spectroscopy (EDS) was carried out at 15 keV. The results are illustrated in the Supplemental Material [36] show the effective substitution and the homogeneous distribution of cobalt throughout the sample. The spatially resolved analysis also confirms a homogenous distribution of cobalt throughout the sample.

**DC magnetic susceptibility.** Temperature dependence of magnetization was measured on a Quantum Design MPMS for a 32.5 mg of polycrystalline Co_{0.03}Mg_{0.97}O synthesized by sol-gel in an external dc field μ₀H_{ext} = 0.1 T. Zero-field-cooling (ZFC) measurements were performed in 2 K steps spaced linearly from 2 to 300 K, while FC measurements were performed in 5 K steps spaced linearly from 2 to 170 K. As described in the Supplemental Material [36], the Curie-Weiss constant was found to be consistent with pairs of Co²⁺ with an exchange interaction reported by Kanamori [16]. The Curie constant was found to agree with a concentration of Co²⁺ ions, consistent with starting concentrations, x-ray powder diffraction, and also EDX measurements. Susceptibility measurements therefore confirm the following key experimental properties of our substituted samples: the lack of magnetic ordering; the absence of measurable clustering of Co²⁺ evidenced from no measurable difference between zero-field and field-cooled sweeps; a Curie-Weiss constant consistent with a dominant 180° superexchange interaction; and finally a Curie constant consistent with starting concentrations.

**Inelastic neutron-scattering details.** 45.8, 45.2, 32.5, and 15.7 g of Co_{0.03}Mg_{0.97}O synthesized by the standard solid-state and sol-gel methods, annealed MgO and CoO, respectively, were placed in separate airtight aluminum cans under helium. The high-energy measurements were made on the direct geometry MARI spectrometer. For measurements concerning the Co_{0.03}Mg_{0.97}O sample synthesized by traditional solid-state methods, MgO and CoO powders, the t 평온계 was operated at 50 Hz in parallel with a Gd chopper spun at frequencies f = 350, 250 and 150 Hz with incident energies E_i = 30, 10, and 5 meV, respectively, providing an elastic resolution of 0.7, 0.2, and 0.1 meV, respectively. For measurements concerning the Co_{0.03}Mg_{0.97}O sample synthesized by sol-gel, the Gd chopper was spun at f = 350 and 250 Hz with an E_i of 29.50 and 14.50 meV, providing an elastic resolution of 0.7 and 0.2 meV, respectively. For both Co_{0.03}Mg_{0.97}O samples, a thick disk chopper with f = 50 Hz reduced the background from high-energy neutrons. A top-loading Displex CCR cooled the samples to a base temperature of approximately 5 K. We note that further neutron inelastic scattering results comparing pure MgO, CoO, and our substituted MgO sample are presented in the Supplemental Material [36].

For lower energies, measurements were made on the in-direct geometry IRIS spectrometer. The final energy was fixed at 1.84 meV by PG002 analyzer crystals in near backscattering geometry. The graphite analyzers are cooled to reduce thermal diffuse scattering, providing an elastic resolution of 17.5 μeV. A combination of IRIS’ long path length and its array of disk choppers allowed us to select multiple time windows, resulting in the measured bandwidth being selectively increased to include energy transfers up to ~2 meV. A top-loading Displex CCR was used to cool the sample to a base temperature of approximately 11 K. For all samples, identical instrumental and environmental parameters were employed on IRIS.

### III. Co²⁺ Pair Interactions

Having discussed the materials preparation and characterization, we conclude that our rocksalt MgO sample substituted with Co²⁺ can be considered to be dominated by pairs of Co²⁺ ions. We now discuss the neutron-scattering response of an isolated pair of magnetic ions and how it can be used to extract both the interaction distance and also the energy-exchange interaction. By considering Co²⁺ pair interactions and only low-energy excitations within the lowest j eff = ½ doublet (with j = βS), the interaction energy scale for a pair of Co²⁺ ions in substituted Mg_{0.03}O is approximated by

\[
\tilde{H}_\text{ex} = 2J \hat{S}_1 \cdot \hat{S}_2 \sim \tilde{a} J \hat{j}_1 \cdot \hat{j}_2,
\]

where \(\tilde{a}\) and \(\tilde{a} = 2β^2\) denote an effective total angular momentum operator with \(j = ½\) and a projection factor, respectively. As summarized by Fig. 1(b), the \(\tilde{H}_\text{ex}\) describes individual j eff = ½ pair excitations as transitions between triplet (Γ eff = 1) and singlet (Γ eff = 0) levels separated by an energy of \(ΔE = \tilde{a} J\) [43-45]. The projection factor \(\tilde{a}\), in this low-energy approximation, can be calculated by diagonalizing \(\tilde{H}_\text{STI} + \tilde{H}_\text{ex}\), with \(\tilde{H}_\text{STI} = 0\) owing to the lack of long-range magnetic order in Co_{0.03}Mg_{0.97}O [17]. This is equivalent to the following Hamiltonian for two (labeled 1 and 2) interacting Co²⁺ ions:

\[
\tilde{H}' = \tilde{a} \hat{j}_1 \cdot \hat{S}_1 + \tilde{a} \hat{j}_2 \cdot \hat{S}_2 + 2J \hat{S}_1 \cdot \hat{S}_2.
\]

By considering \(I = 1\) and \(S = \frac{3}{2}\), this amounts to 144 basis states and a 144 × 144 matrix for this particular Hamiltonian in terms of the two-particle basis of \(|\tilde{J}_z, m_{\tilde{J}_z}, s_1, m_{s_1}, s_2, m_{s_2}|\) \(\otimes\)
with \( |F(|Q|)|^2 \) the magnetic form factor. Since the modulation is solely dependent on the intrapair distance \( \mathbf{R}_m \), the excitation can be assigned to a particular pair and corresponding coordination shell in the \( \text{Fm} \tilde{3} \text{m} \) structure, as illustrated in Fig. 1(a).

IV. RESULTS AND DISCUSSION

Having discussed the theory for isolated pairs in dilute \( \text{Co}_{0.03}\text{Mg}_{0.97} \text{O} \), we now present the experimental data. As illustrated by Fig. 2(a), low-temperature/incident-energy inelastic neutron spectroscopic measurements on powder \( \text{Co}_{0.03}\text{Mg}_{0.97} \text{O} \) display a hierarchy of dispersionless excitations up to \( \Delta E \sim 15 \text{ meV} \). Based on the energy value of the excitations, we can assign an exchange constant as shown in Fig. 2(b) using the previously measured value for the spin-orbit-coupling constant \( \lambda \) [17] for isolated \( \text{Co}^{2+} \) on a rocksalt lattice. The intensities for each of the seven excitations in Fig. 2(a) exhibit a modulated \( |Q| \) dependence, characteristic of pairwise interactions and thus distinguishing them from single-ion dispersionless crystal-field excitations [43]. As shown in Figs. 3(a) and 3(b), by fitting the intensity of each mode at different energies to Eq. (5), the different pair excitations could be assigned to relative coordination shells ranging from \( m = 1 \) to \( m = 4 \).

We now discuss the temperature dependence with the goal of extracting the sign of \( J \). Antiferromagnetically coupled \( (J > 0) \) pairs of \( j_{\text{eff}} = \frac{1}{2} \) spins consist of a singlet ground state and a triplet excited state, while ferromagnetic coupling \( (J < 0) \) gives a triplet ground state and a single excited state. These two different coupling scenarios give distinct temperature dependences of the integrated intensity that scales as the thermal population difference between the ground and excited states [51,52], with antiferromagnetic pairs following

\[
I_{\text{AF}}(T) \propto (1 - e^{-\Delta E/|k_B|T})/(1 + 3e^{-\Delta E/|k_B|T}),
\]

and ferromagnetic pairs following

\[
I_F(T) \propto (1 - e^{-\Delta E/|k_B|T})/(3 + e^{-\Delta E/|k_B|T}),
\]

such that as \( T \to 0 \) K, the ratio

\[
\frac{I_{\text{AF}}}{I_F} = \frac{3 + e^{-\Delta E/|k_B|T}}{1 + 3e^{-\Delta E/|k_B|T}} \to 3.
\]

As illustrated in Fig. 3(d), by normalizing the temperature dependence by \( I_F(T) \), all integrated intensities fall onto either one of two universal curves describing antiferromagnetism or ferromagnetism.

All extracted values of \( J \) based on the energy, momentum, and temperature dependence discussed above are summarized in Table I. All coordination shells, with the exception of \( m = 2 \), display two closely spaced excitations with differing signs for the exchange constant, as illustrated in Fig. 3(c) for the \( \sim 5 \text{ meV} \) excitation. This presence of dual ferro- and antiferromagnetic interactions for \( m = 1, 3, \) and 4 is consistent with the GKA rules [40–42,53] since each of these exchange pathways consists of at least one \( 90^\circ \) \( \text{Co}^{2+} - \text{Co}^{2+} \) interaction involving the overlap of half and filled orbitals. Indeed, the GKA rules predict that the combination of the orbital degree of freedom for each \( \text{Co}^{2+} \) and a lack of orbital ordering (or anisotropy) would manifest itself as either a direct antiferromagnetic \( t_{2g} - t_{2g} \) or a weaker ferromagnetic

\[
\langle \hat{H}_{\text{pair}} \rangle \frac{J_{\text{eff}}}{J} \propto \frac{J_{\text{eff}}}{J} \frac{\Delta E}{|k_B|T} \sim \frac{J_{\text{eff}}}{J} \frac{\Delta E}{|k_B|T} \to 3.
\]

\[
\frac{I_{\text{AF}}}{I_F} = \frac{3 + e^{-\Delta E/|k_B|T}}{1 + 3e^{-\Delta E/|k_B|T}} \to 3.
\]

\[
\langle \hat{H}_{\text{pair}} \rangle \frac{J_{\text{eff}}}{J} \propto \frac{J_{\text{eff}}}{J} \frac{\Delta E}{|k_B|T} \sim \frac{J_{\text{eff}}}{J} \frac{\Delta E}{|k_B|T} \to 3.
\]
FIG. 3. (a) Constant-$E$ cut ($\Delta E = [12,14]$ meV) from MARI at 5 K with an $E_i = 30$ meV. The green curve is a fit to Eq. (5) with $|R|_1 = 4.2(3)$ Å ($m = 2$ pairs). The red curve is with $|R|_1$ fixed as 2.98 Å ($m = 1$ pairs). (b) Scaled and form-factor-corrected $|Q|$ dependence of the intensities for all magnetic excitations with $|R|$ calculated from the fitting routine described in (a). The solid black curve is $1 - \sin(|Q| R_{i0})/|Q| R_{i0}$. (c) Constant-$Q$ cut (MARI, $E_i = 10$ meV) showing a different temperature dependence for the two peaks despite both being from $m = 1$ pairs. (d) Normalized temperature dependence of the Bose-factor-corrected integrated intensity for all seven excitations (Fig. 2) showing two universal curves calculated (dashed lines) for antiferromagnetic and ferromagnetic coupling. Both the integrated intensities and the calculated behavior of antiferromagnetic or ferromagnetically coupled pairs were normalized by $I_0(T)$, as described in the main text. The inset is a pictorial representation of the sign of $J$ as predicted by the GKA rules [40–42]—antiferromagnetism (left) is a result of exchange between two half-filled and completely filled $t_{2g}$ orbitals, while weaker ferromagnetism (right) is a result of exchange between a half-filled and completely filled $t_{2g}$ orbitals. Yellow arrows denote local $t_{2g}$ spin configurations and teal arrows denote total spin configurations on each Co$^{2+}$.

$t_{2g}^1 - t_{2g}^2$ exchange interaction. As summarized in Fig. 3(d) and Table I, the experimental results verify the GKA rules [40–42,53] as the antiferromagnetic interaction is stronger than the ferromagnetic alternative for all the $m \neq 2$ excitations, while the $180^\circ$ Co$^{2+} - O^{2-} -$ Co$^{2+} m = 2$ coupling leads to only a strong antiferromagnetic interaction.

Having assigned the signs of the seven exchange constants for dilute Co$_{0.03}$Mg$_{0.97}$O, we now provide a comparison with thermodynamic data and previously measured and calculated exchange constants for bulk CoO. The additional complication of dual ferro- and antiferromagnetic interactions for most $m$ exchange pathways in combination with the entanglement of individual spin-orbit manifolds in the presence of magnetic order provides a possible explanation for the large range of $J$ values reported for CoO [16,30,31,35,54–58]. As summarized in Table I, the values of $J$ show good agreement with three general trends reported by experiment [30]: (i) dominant $J_2 > 0$, (ii) a $J_1 < 0$, and (iii) a significantly smaller but non-negligible $J_3$, all in broad agreement with the trends concluded from a recent generalized gradient approximation (GGA)+$U$ density functional theory (DFT) calculation on CoO (though no such dual exchange was predicted) [32]. In terms of thermodynamic data, the Curie-Weiss constant is related to the exchange interactions via $\Theta_{CW} = -\frac{1}{2} \sum_i z_i J_i$, where the spin value $S = \frac{3}{2}$ and $z_i$ is the number of neighbors for each $i$th exchange interaction [48,49]. Following Kanamori [16] and applying a correction for spin-orbit coupling, the effective Curie-Weiss temperature $\tilde{\Theta}_{CW}$ is listed in Table I and compared against a mean-field $T_N$ calculated based just on $J_2$. The estimated $\tilde{\Theta}_{CW}$ of $-295(5)$ K ($-25.4(5)$ meV) and a mean-field estimate of $T_N$ of $283(5)$ K [24.4(3) meV] demonstrate close similarities with experimentally determined values of $\tilde{\Theta}_{CW} = -330(4)$ K [46,47] and $T_N = 291(4)$ K [25], respectively, for CoO. The excellent agreement results from the near-perfect cancellation of antiferromagnetic and ferromagnetic interactions for all coordinations with the exception of $m = 2$ (the $180^\circ$ interaction). Although the Co$_{0.03}$Mg$_{0.97}$O lattice ($a = 4.21$ Å) is contracted relative to that of pure CoO ($a = 4.26$ Å), the above agreements of energy scale are highly suggestive that the Co$^{2+} -$ Co$^{2+}$ exchange interactions are not greatly
TABLE I. Magnetic exchange constants for CoO determined by the current study, magnetic exchange constants for CoO as cited in literature [30,31], and calculated for CoO by Deng et al. [32] using GGA+$U$ DFT. The values from GGA+$U$ DFT have been renormalized such that $J_z$ is equal to the value from this current study. The values of $T_N$, $\theta_{\text{CW}}$, and $\lambda$ reported in the literature [17,25,46,47] for CoO have been included for the purposes of a comparison to the mean-field value [48,49] of $\theta_{\text{CW}}$ corresponding to the $J$ values determined by the current study. The results demonstrate that in the case of an orbital degeneracy in the $t_{2g}$ channel, dual ferro- and antiferromagnetic interactions occur with comparable magnitudes.

<table>
<thead>
<tr>
<th>Quantity/Source</th>
<th>Current study (meV)</th>
<th>Literature studies (meV)</th>
<th>Calculated (meV) [32]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>24(5) [17]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_{1AF}$</td>
<td>1.000(8)</td>
<td>0.60 to $\sim$ 0.31 [16,30]</td>
<td>$-0.97(2)$</td>
</tr>
<tr>
<td>$J_{1F}$</td>
<td>$-0.918(6)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_z$ or $J_{2AF}$</td>
<td>3.09(5)</td>
<td>2.8 to 0.0013 [30]</td>
<td>3.09(5)</td>
</tr>
<tr>
<td>$J_{1AF}$</td>
<td>0.258(1)</td>
<td>$-0.67$ [31]</td>
<td>$-0.461(8)$</td>
</tr>
<tr>
<td>$J_{1F}$</td>
<td>$-0.182(1)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_{1AF}$</td>
<td>0.0759(4)</td>
<td></td>
<td>$-0.0085(1)$</td>
</tr>
<tr>
<td>$J_{1F}$</td>
<td>$-0.0504(4)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_N$</td>
<td>24.4(3)$^a$</td>
<td>25.1(4) [25]</td>
<td></td>
</tr>
<tr>
<td>$\theta_{\text{CW}}$</td>
<td>$-25.4(5)$</td>
<td>$-28.4(4)$ [46,47]</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Calculated using the mean-field estimate $T_N \sim |\frac{1}{2} S(S+1)z_2 J_z|$.

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