Electronic structure, chemical bonding, and magnetic properties in the intermetallic series Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_2$B$_2$ from first principles

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First-principles, density-functional studies of the electronic structure, chemical bonding, ground-state magnetic ordering, and exchange-interaction parameters have been performed for the entire Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_2$B$_2$ series of magnetic compounds. The results indicate that their magnetic properties depend in an extremely sensitive way on the degree of band filling and bandwidth. Continuous substitution of Ru by Rh changes the ground state from an antiferromagnet to a ferromagnet, as well as increases the effective spin moment caused by filling the bands with five additional electrons per formula unit together with a narrowing of the 4$d$ band. The correlations between the character of the chemical bonding and the resulting exchange couplings are discussed. The enhancement of Fe-Fe exchange coupling caused by Rh/Ru atoms is estimated. Trends for the macroscopic ordering temperatures are correctly reproduced.

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I. INTRODUCTION

During the last decade, a number of quaternary intermetallic borides with the general formula $M_2M'T_xB_2$ ($M$=Mg or Sc; $M'$=main-group metal or 3$d$ element; $T$=Ru, Rh, Ir) crystallizing in the space group $P4/mmm$ have been synthesized and structurally characterized.1–3 Among these compounds, those with magnetically active 3$d$ elements Mn, Fe, Co have attracted increased interest because they exhibit ferromagnetic or antiferromagnetic behavior that can be fine-tuned by synthetic means. In addition, the magnetically active 3$d$ metal atoms form well separated, one-dimensional chains. Thus, the question arises whether these compounds show low-dimensional, itinerant magnetism, which offers potential application for data storage and retrieval.

From a theoretical perspective, the use of quantum-chemical bond detecting tools such as the crystal orbital hamilton population (COHP)4 analysis made it possible to understand, from a chemical perspective, the nature of the magnetic behavior in some of these compounds as it was shown to be solely a function of the electron count.5 Among $M_2M'T_xB_2$ examples, ferromagnets turned out to have 65 valence electrons (e.g., Sc$_2$FeRh$_2$B$_2$) with the Fermi level falling within metal-metal antibonding states, whereas antiferromagnets, e.g., Mg$_2$MnRh$_2$B$_2$, have 62 valence electrons, where the Fermi level falls within metal-metal nonbonding states. These findings also allowed further experimental search for new ferromagnets and antiferromagnets, and successfully led to the discovery of both Sc$_2$MnRu$_2$Rh$_2$B$_2$ and Sc$_2$FeRu$_2$Rh$_2$B$_2$. These derivatives are conveniently formulated as $M_2M'(T_1, xT')_xB_2$, so that there is chemical choice among the 4$d$ (T, T$'$) metal sites to adjust the number of valence electrons. These two isotypic compounds both contain 62 valence electrons and, as predicted, both are itinerant antiferromagnets.5,6

The magnetic properties and exchange couplings of related magnetic systems, i.e., FeRh and FePt, have been studied7–9 and provide differing opinions on how to treat the Rh or Pt magnetic moments in such systems. The results of noncollinear magnetic calculations7,8 show that the magnetic moment at the Fe site is essentially localized and can be described according to a rigid-spin approximation, while the Rh or Pt magnetic moments are delocalized and determined, both in direction and magnitude, by the exchange field from the Fe moments. To describe these systems with both localized and delocalized magnetic degrees of freedom, an effective spin Hamiltonian model was developed.7,8 In this model, the localized Fe magnetic moments are described by a Heisenberg Hamiltonian and the itinerant moments within a Stoner model, in which the magnetic moments of Rh or Pt atoms are induced by the Fe exchange field. This description quantitatively reproduces the experimentally observed anomaly in the temperature dependence of the magnetic anisotropy energy. On the other hand, a standard Heisenberg model with rigid spins for both Fe and Rh moments in FeRh reproduced the phase transition temperatures of both antiferromagnetic-to-ferromagnetic and ferromagnetic-to-paramagnetic phase transitions in reasonable agreement with experiment.9

In the present publication, we investigate the local nature of the exchange interactions in Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_2$B$_2$ to examine the relationship between effective exchange coupling and metal-metal COHP in these itinerant magnets. Our calculations of exchange couplings are based on the linear-response technique10–13 in the long wavelength approximation.14 Two models are used to describe the magnetic properties of Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_2$B$_2$. In the first case (“model 1”), we treated the magnetic moments at both the Fe and Rh/Ru sites as independent rigid moments together with the usual assumption of weak enhancement of magnetic exchange parameters $(J_{ij})$.1,4 We obtain $J_{ij}$ values for a number of Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_2$B$_2$ compounds from first principles, and then analyze how the mechanism of the magnetic coupling depends on electronic structure variations induced by atomic substitution. In particular, we will arrive at results that are similar to our previous treatments for Heusler alloys15 and to published results for FePt and FeRh.7–9 In Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_2$B$_2$, the 4$d$-3$d$ Rh/Ru-Fe interactions yield...
larger, even leading contributions to the total effective coupling of the Fe atoms as compared to the 3d–3d Fe–Fe interactions. In the second model (“model 2”), we treated just the Fe magnetic moments as independent. However, to calculate the Fe–Fe exchange parameters, we used the total magnetic susceptibility $\chi_{ij}^{(0)}$, rather than the “bare” magnetic susceptibility $\chi_{ij}$, which has been traditionally used for such calculations. In this case, the total susceptibility $\chi_{ij}^{(0)}$ includes enhancement effects caused by Rh/Ru sites.

Finally, numerical calculations targeted at finite-temperature properties such as Curie ($T_C$) and Néel ($T_N$) ordering temperatures are performed on the basis of a direct, exchange-based approach. Because the mean-field approximation (MFA) usually overestimates critical temperatures in systems with few nearest neighbors, we also used the cluster variation method (CVM)\textsuperscript{16,17} to calculate critical temperatures for some concentrations. CVM typically gives agreement within 5%–10% with results of more accurate spin dynamics procedures, even in such a systems such as dilute magnetic semiconductors,\textsuperscript{17} where MFA overestimates $T_C$ by a factor of 2.

In summary, this contribution attempts to provide an essentially chemical understanding of bonding and magnetic exchange parameters starting from ideas touching upon elementary body-centered cubic 3d metals such as α-Fe and continuing these ideas for the quaternary intermetallic borides as done in Refs. 15 and 18.

II. CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

All quaternary intermetallic borides with the general formula $M_2M'T_3B_2$ (Refs. 1–3) crystallize with an ordered variant of the Ti$_5$Co$_5$B$_2$ aristotype.\textsuperscript{10} As shown in Fig. 1, this structure contains trigonal, tetragonal, and pentagonal prisms of the $T$ (Co) atoms stacked on top of each other along the [001] direction. The trigonal prisms enclose the B atoms, while the pentagonal prisms accommodate the $M$ atoms and the tetragonal prisms (cubes) contain the $M'$ atoms. The $M'$ atoms are arranged in chains along the [001] direction (see Fig. 1, right) with intrachain $M'$–$M'$ distances of about 3.0 Å and interchain distances of about 6.6 Å.\textsuperscript{19}

The electronic structures of Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_3$B$_2$ were calculated using the tight-binding, linear muffin-tin orbital method with the atomic-spheres approximation (LMTO-ASA).\textsuperscript{20,21} The exchange-correlation term was calculated both within the local-spin-density approximation (LSDA), which was parametrized according to von Barth and Hedin,\textsuperscript{22} and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional\textsuperscript{23} for the experimental values of the lattice parameters. A mesh of 54 $k$ points in the irreducible wedge of the Brillouin zone (BZ) turned out to be sufficient for the calculations of the exchange parameters. To treat different concentrations of Ru and Rh quantitatively, we used ordered distributions of these elements within the experimental unit cells. The sizes of atomic sphere radii for our calculations are Ru1/Rh1, 2.70–2.72 Å; Ru2/Rh2, 2.60–2.62 Å; Sc, 3.31–3.20 Å; Fe, 3.12–3.04 Å; B, 2.17–2.15 Å.

The chemical bonding was investigated using the COHP analysis, which is an energy-resolved partitioning technique of the band-structure energy (sum of the Kohn-Sham eigenvalues) in terms of atomic and bonding contributions. After the electronic structure calculations have been brought to full self-consistency, an energy-partitioning method is utilized to separate the entire band-structure energy into specified interatomic interactions (the COHP) given that an atom-centered basis set (such as LMTOs) has been provided. In other words, the delocalized electronic structure calculated in reciprocal space is exactly transformed into real space; in addition, the result of this transformation is presented in an energy-resolved form, i.e., as a function of band filling. Experience shows that, within stable materials, nature maximizes the integrated COHP values for the strongest bonds by annihilating antibonding states such as to avoid Jaehn-Teller or Peierls instabilities.

For the prediction of ferro—or antiferromagnetic spin ordering in magnetic intermetallics, the COHP is calculated using a non-spin-polarized state and analyzed for the highest filled states, i.e., at the Fermi level. Whenever atom-atom interactions turn out to be strongly antibonding at the Fermi level for those metals which show strong exchange splitting (i.e., the 3d metals), the material is likely to spin polarize and order ferromagnetically, as seen for α-Fe [body-centered cubic (bcc)]. If the atom-atom interactions are nonbonding at the Fermi level (such as in bcc-Cr), the material will exhibit antiferromagnetic ordering.

The general theoretical strategy to evaluate the local effective exchange parameters in the long wavelength approximation with an assumption of weak enhancement\textsuperscript{14} has already been discussed in Ref. 24. These effective exchange parameters are used to calculate the thermal properties\textsuperscript{11} of magnets, and are derived from the pairwise exchange interactions, $J_{ij}$, which explicitly enter the Heisenberg Hamiltonian,

$$
H = -\sum_{i,j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j,
$$

where $i$ and $j$ are indices of atoms, and $\mathbf{e}_i$ and $\mathbf{e}_j$ are the directions of the local magnetic moments at atoms $i$ and $j$.

For model 1, the $J_{ij}$ values are obtained using multiple scattering theory according to
\[ J_{ij} = \frac{1}{2\pi} \int d\epsilon \text{Im} \sum_{L,L'} \left\{ \delta P_{ij}(\epsilon) [T^{\dagger}_{L',L}(\epsilon)T^i_{L,L'}(\epsilon) + T^{\dagger}_{L',L}(\epsilon)T^i_{L,L'}(\epsilon)] \delta P_{jL}(\epsilon) \right\}, \]

where \( \delta P_{ij}(\epsilon) \) is the on-site perturbation on atom \( i \) for orbital momentum \( l \) and \( T^{\dagger}_{L}(\epsilon) \) is the scattering-path operator connecting atoms \( i \) and \( j \), dependent on the complex energy \( \epsilon \) for the channel with spin \( \sigma \) (\( \uparrow \) or \( \downarrow \)) and \( L \) stands for the orbital momentum and its projection \((l,m)\). Details of this calculation are summarized in Appendix A. For the assumption for on-site Rh/Ru exchange coupling. I/H9254

The static transverse susceptibility change couplings calculated before enhancement; \( J_{ij} \) for Ru,27 and Stoner exchange integral, i.e., \( J_{ij} = -\delta^2 E/\delta \alpha_i \delta \alpha_j \), with respect to either ferromagnetic (FM) or antiferromagnetic (AFM) arrangements of magnetic moments. From this perspective, \( J_{ij} \) will be possible valued for the stable magnetic state and negative valued for the unstable one.

The exchange parameters \( J_{ij} \) (model 1) or \( \tilde{J}_{ij} \) (model 2) are used for the calculation of transition temperatures \( T_c \) or \( T_N \) in the mean-field approximation as a largest solution of the equation

\[ \det \left( \frac{2}{3}(J_{ij})_{nm} - T \delta_{nm} \right) = 0, \]

where \( n \) and \( m \) are the indices of the inequivalent magnetic sublattices, and \( (J_{ij})_{nm} \) is an effective exchange interaction between one atom from sublattice \( n \) with all atoms from sublattice \( m \).28,29 i.e., \( (J_{ij})_{nm} = \sum_{\alpha} \omega_{ij}(k) \) (or \( \tilde{J}_{ij} \)), for a summation over all atoms \( j \) in the magnetic sublattice \( m \).

To investigate the dimensionality of the magnetic system in \( \text{S}_2\text{Fe}(\text{Ru}_{1-x}\text{Rh}_x)\text{B}_2 \), spin wave dispersion curves, \( \omega_\alpha(k) \), were calculated.30 This result can be confirmed by inelastic neutron scattering experiments. The expression for the calculation of \( \omega_\alpha(k) \) from the calculated \( J_{ij} \) parameters is described in Appendix B.

### III. RESULTS AND DISCUSSION

#### A. bcc 3d metals

We start our analysis with nonmagnetic, bcc iron and the 3d series of the magnetic elements. The COHP curve for the nearest neighbor interactions as a function of the number of \( d \) electrons (see Ref. 31 for more details), as well as the effective total exchange parameter \( J_0 \) as a function of the band filling, is presented in Fig. 2 (in this case, there is a single effective exchange parameter). These figures are based on a self-consistent calculation of bcc-Fe itself, where the change in the valence electron number \( N \) is introduced solely by a rigid-band approach.

A systematic change occurs in the nearest neighbor COHP and \( J_0 \) as a function of the \( d \) band filling.25 Whenever the number of valence electrons per atom is smaller than 7.5, such as in manganese or chromium, the FM state is no longer stable \((J_0 < 0)\). This result agrees well with experiment and also correlates with the nearest neighbor COHP interpretation [ferromagnetism for the Fermi level \((E_F)\) positioned in antibonding states, and antiferromagnetism when \( E_F \) is located among nonbonding states]. Thus, the COHP interpretation identifies chromium as an ideal antiferromagnet where \( E_F \) exactly separates bonding states from antibonding states.

To demonstrate the general character of this result, we calculated the variation of \( J_0 \) with band filling for a model rectangular density of states (DOS; see Fig. 3). For such a DOS, all potential parameters, except the center of the band interactions between the magnetic moment of atom \( i \) and the magnetic moments of all other atoms determine the effective exchange parameter at atom \( i \), \( (J_{ij}) = \sum_j J_{ij} \), also equals the second derivative of the total energy relative to angular deviations from an initially collinear configuration of magnetic moments, i.e., \( (J_{ij}) = \delta^2 E/\delta \alpha_i \delta \alpha_j \), with respect to either ferromagnetic (FM) or antiferromagnetic (AFM) arrangements of magnetic moments. From this perspective, \( J_{ij} \) will be possible valued for the stable magnetic state and negative valued for the unstable one.

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(C_i), are equal for spin up and down. In this case the expression for J_0 [see Eq. (A5) in Appendix A] can be reduced to the form

$$J_0(E_F) = \frac{1}{2\pi} \int dE \text{Im} \sum_{l,l'} [\Delta_l(G_{l,l'}^r - G_{l,l}^r)]$$

$$+ 2\Delta_l G_{l,l'}^r \Delta_l G_{l,l'}^s$$,

(7)

where $\Delta_l = (C_l - C_l)/2$ is the splitting between spin up and down bands and $G_{l,l'}^\sigma(E)$ is the usual Green’s function for spin $\sigma$ and a single site in the unit cell

$$G_{l,l'}^\sigma(E) = \sum_\nu \int d\mathbf{k} \frac{X_{\nu l'}^\sigma(\mathbf{k}) X_{\nu l}^\sigma(\mathbf{k})^*}{\epsilon - e_\nu^\sigma(\mathbf{k})}$$,

(8)

where $X_{\nu l'}^\sigma(\mathbf{k})$ and $e_\nu^\sigma(\mathbf{k})$ are, respectively, the eigenvectors and eigenvalues of the Schrödinger equation. Using the relationship between the Green’s function and the partial density of states, $N_{\nu l}(E) = -\frac{1}{\pi} \text{Im} G_{l,l}^\sigma(E+i0)$, Eq. (7) can be reduced to the form

$$J_0(E_F) = \Delta_l M_l(E_F) - 2\Delta_l \chi_{l,l'}^r(E_F) \Delta_l$$,

where $M_l(E_F)$ is the magnetic moment at $E_F$ corresponding to the $l$ band and $\chi_{l,l'}^r(E_F)$ is the corresponding static transverse susceptibility. The first contribution to $J_0(E_F)$ $\Delta_l M_l(E_F)$, shown by the dotted green line in the lower graph of Fig. 3, linearly increases from the bottom of the spin up band at $-3$ eV to the bottom of the spin down band at $-1$ eV, then remains constant to the top of the spin up band at $+1$ eV (between $-1$ and $+1$ eV, the difference between the spin up

and spin down partial DOS is zero), and finally linearly decreases to zero at the top of the spin down band at $+3$ eV. The second contribution, $2\Delta_l \chi_{l,l'}^r(E_F) \Delta_l$, shown by the dashed blue line, is the “self-exchange” term. This analysis indicates that $\Delta_l M_l(E_F)$ exceeds $2\Delta_l \chi_{l,l'}^r(E_F) \Delta_l$ near the bottom and top of this rectangular DOS, but that $2\Delta_l \chi_{l,l'}^r(E_F) \Delta_l$ exceeds $\Delta_l M_l(E_F)$ around the middle of the band. The two terms are exactly equal at the partial spin up and spin down DOS boundaries. When $J_0(E_F) > 0$ (for $-3$ eV $< E_F < -1$ eV and $+1$ eV $< E_F < +3$ eV), FM ordering is stable, whereas for $J_0(E_F) < 0$ (for $-1$ eV $< E_F < +1$ eV), AFM ordering is stable. Therefore, the ground state of a system with a nearly empty or filled band is FM, and AFM for nearly half filled. In this model, we did not use any information about the band’s character, i.e., crystal structure effects or specific atomic orbitals, e.g., $d$ states. Nevertheless, regions of the DOS near band centers are generally nonbonding; strong bonding or antibonding interactions occur, respectively, at the lower and upper bounds of the DOS. Furthermore, the Stoner criterion must be satisfied for the existence of the magnetic state.

Variation in $J_0(E_F)$ with respect to band filling from the $t_{2g}$ bands in the bcc 3d metals (using Fe for the calculation) is similar to the rectangular band picture, as shown in Fig. 4; the variation in $J_0(E_F)$ from the $e_g$ states is close to the $t_{2g}$ curve. In general, the picture for bcc transition metals is close to the result presented for the model calculation, but there are some differences in the shape of the $J_0(E_F)$ curve determined by the differences in shapes of the respective DOS curves.

**B. Sc₂Fe(Ru₁₋ₓRhₓ)₃B₂**

The numerical results for the entire Sc₂Fe(Ru₁₋ₓRhₓ)₃B₂ series are presented in Tables I and II, which summarize the
calculated values of the local magnetic moments, the total energy differences between the FM and AFM states, the effective exchange parameters, as well as the ordering temperatures. The magnetic moments on the Sc, Rh1, and B atoms are negligibly small and are not included in the table.

For Sc$_2$FeRh$_6$B$_2$ ($x=1$), the calculated Fe magnetic moment equals 3.4 $\mu_B$ using the LSDA approach (3.5 $\mu_B$ with the GGA), which is much larger than in bcc Fe (2.2 $\mu_B$). Due to strong mixing between the Fe 3$d$ orbitals with the 4$d$ orbitals of the eight nearest Rh2 neighbors, a significant spin polarization at the Rh2 atoms (0.25 $\mu_B$ in LSDA; 0.27 in GGA) results (see partial DOS shown in Fig. 5). This polarization is also reflected in nonzero $(J_0)_{Rh2}$ values of 11 meV. For comparison, the $(J_0)_{Fe}$ value corresponds to 65 meV. In general, the GGA gives larger magnetic moments compared to LSDA results, which is similar to results for bulk 3$d$ magnetic metals Fe, Co, and Ni, as well as larger exchange parameters $-12$ and 79 meV, correspondingly, for $(J_0)_{Rh2}$ and $(J_0)_{Fe}$. Upon reducing the number of valence electrons on going from Sc$_2$FeRh$_6$B$_2$ (65 electrons) to Sc$_2$FeRu$_6$B$_2$ (60 electrons), all moments and exchange parameters become smaller. The $T_C$ or $T_N$ ordering temperatures were calculated according to the MFA (in the system with two magnetic atoms per cell) using Eq. (6); the corresponding effective exchange interactions for the different sublattices $(J_0)_{sub}$, which are used in Eq. (6), are listed in Table II. The theoretical Curie temperature $T_C$ of Sc$_2$FeRh$_6$B$_2$ obtained from LSDA exchange parameters equals 270 K, a value which underestimates the experimental result by nearly 200 K; the GGA result is 335 K and remains significantly smaller than the experimental value. The results in Table I also reflect the usual underestimation of the Curie temperatures for the entire series, just as for the related class of full Heusler alloys.

As we mentioned in the first two sections, the model of rigid spins at Rh/Ru sites in systems related to the Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_3$B$_2$ series is limited. To compare our initial MFA results, we used the effective spin Hamiltonian model, in which rigid moments are assigned to Fe atoms only, moments which interact through effective exchange parameters, $\tilde{J}_{ij} = J_{ij} + (\frac{1}{2}I_{a}\chi_{a}^{2})\sum_{\alpha}\rho_{\alpha}^{i}\rho_{\alpha}^{j}$, where $J_{ij}$ is the bare Fe-Fe exchange interaction, $I_{a}$ is the Stoner parameter for Ru or Rh, $\chi_{a}$ is the Rh/Ru longitudinal susceptibility, $-4 \times 10^{-4}$ meV$^{-1}$ (estimated from the Rh/Ru partial density of states at the Fermi energy), and index $\alpha$ corresponds to Rh/Ru atoms. The coefficient in front of the summation over $\alpha$, $(\frac{1}{2}I_{a}\chi_{a}^{2})$ in the expression for $\tilde{J}_{ij}$, is $6 \times 10^{-5}$ meV$^{-1}$, a value which suppresses the contributions from Fe-Rh/Ru interactions to $\tilde{J}_{ij}$ in the Sc$_2$Fe(Ru$_{1-x}$Rh$_x$)$_3$B$_2$ family of compounds. As a result, $T_C$ obtained from this effective Heisenberg model is even smaller compared to a rigid Rh/Ru spin model. Results in better agreement with experiment come from model 2. The enhancement produced by the Rh/Ru magnetic subsystem increases $(J_0)_{Fe}$ to 57 meV and the subsequent MFA result for $T_C$ is 440 K; the corresponding CVM result is 350 K. For systems with small numbers of nearest neighbors, Curie temperatures predicted by the MFA typically exceed those calculated by other, more accurate models, e.g., CVM or Monte Carlo. Although models 1 and 2 underestimate the experimental Curie temperature ($\sim 450$ K), model 2 is a distinct improvement through the enhancement of the Rh/Ru subsystem. Higher accuracy cannot be achieved using the proposed formalism.

The DOS plot of Sc$_2$FeRh$_6$B$_2$ together with the partial DOS curves (LSDA result) is presented in Fig. 5. The 3$s$ states of the boron atoms occur between $-10.9$ and $-8.2$ eV and are separated from the conduction band by a 1.4 eV gap. Figure 5 also indicates larger magnetic polarization of the Rh2 sites as compared to the Rh1 atoms around the Fermi energy, an effect which is induced by Fe atoms. Preference for the FM ground state of Sc$_2$FeRh$_6$B$_2$ ($x=1$) can also be extracted from the numerical results listed in Table I; the AFM state lies higher in energy by 536 K in LSDA (631 K in GGA), but is stable with respect to small fluctuations of the direction of the spin moment, i.e., $(J_0)_{Rh2}^{(AFM)}$, $(J_0)_{Rh2}^{(AFM)} > 0$. In such a case, it is possible to find metamagnetic transitions from a FM state at low temperature to an AFM state at a somewhat higher temperature, and then to the paramagnetic state.

Figure 6 illustrates the course of the effective exchange parameters $(J_0)_{Fe}^{(FM)}$ as a function of the band energy for the phases Sc$_2$FeRh$_6$B$_2$ ($x=1$) and Sc$_2$FeRu$_6$B$_2$ ($x=0$) calculated in LSDA using model 1. The GGA does not change our results significantly and model 1 provides a relevant description of the stability of FM and AFM orders. Figure 6 also shows the partial DOS of the Fe and Rh2 (or Ru2) atoms in the two compounds. Clearly, these curves are quite similar in shape but not in magnitude, and the different valence electron counts (depicted as solid and dashed Fermi levels in Fig.
TABLE I. Calculated and experimental results for $\text{Sc}_2\text{Fe(Ru/Rh)}_x\text{B}_2$ ($0 \leq x \leq 1$): (i) the total energy difference $\Delta E$ (K/unit cell) between the FM and AFM ordered states ($\Delta E = E_{\text{FM}} - E_{\text{AFM}}$), (ii) local magnetic moments ($\mu_B$), and effective exchange parameters (meV) for Fe ($2 \times$) and Rh/Ru ($8 \times$) sites in FM and AFM ordered (MO) states; and (iii) ordering temperatures, $T_C$ or $T_N$ (K), calculated in the MFA using LSDA and GGA, compared with the experimental values (Expt.) and values obtained by “model 2 (M2),” in which we add Rh/Ru enhancement to Fe exchange parameters. The labels “unst” in the MFA columns means that the corresponding magnetic ordering is unstable, i.e., $(J_0) < 0$; “—” in the Expt. column indicates this type of ordering is not observed experimentally. The Néel temperature for $x = 0.4$ is not known.

<table>
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<th>$x$ (N)</th>
<th>$\Delta E$ (K)</th>
<th>MO</th>
<th>Class</th>
<th>$\mu_B$</th>
<th>$T_C$ or $T_N$ (K)</th>
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<td>148</td>
</tr>
</tbody>
</table>

$^a$Reference 24.

6) make $\text{Sc}_2\text{FeRh}_x\text{B}_2$ a ferromagnet and $\text{Sc}_2\text{FeRu}_x\text{B}_2$ an antiferromagnet. The crossover between FM and AFM ordering is reached at a valence electron count of 63 electrons; below this number, AFM ordering is preferred. The same result can also be inferred from Fig. 7, which shows the variations of $J_{ij}$ as a function of the valence electron count, and is in perfect agreement with the COHP picture. Figure 7 (middle) directly displays the energy difference between the FM ($N = 64$ or 65 electrons) and the AFM ($N = 60–63$ electrons) states.

As we have already mentioned, the pair exchange interactions $J_{ij}$ are not entirely localized between the Fe atoms (see Table II), despite the fact that the largest $J_{ij}$ values correspond to the interactions of two nearest Fe neighbors and are, respectively, 10 and 1.6 meV in LSDA (13 and 0.5 meV in GGA). Exchange interactions between different Fe chains (entries 3 and 5 in Table II) are almost zero such that the chemical picture of almost isolated one-dimensional (1D) Fe chains (see Fig. 1, left) seems, at first glance, justified. Nonetheless, there are significant Fe-Rh2 exchange interactions, which may be understood from the relatively large spin polarization induced on Rh2 sites because of the short Fe-Rh2 distance. In fact, the total contribution from the eight neighboring Rh2 atoms to the effective exchange parameter $(J_0)_{\text{Fe}}$ is larger than the bare Fe-Fe contribution.

The chemical picture of almost isolated 1D Fe chains raises a very important question about whether this system should be discussed as a 1D magnetic system. This question is important because of the fact that a 1D magnetic chain described by an isotropic classical Heisenberg model does not have long range order at any temperature. An answer could be obtained from magnon dispersion curves, $\omega_n(k)$. In
TABLE II. Pairwise exchange parameters \( J_{ij} \) (meV) for Fe-X pairs (index \( i=\text{Fe} \)), \( R/a \) being the relative interatomic distance, \([R_i/a_i,R_j/a_j,R_k/c]\) the corresponding vector, \( M \) is the number of equivalent pairs, and \((J_{ij})_{im}\) is the effective exchange parameters. \( M1=\text{“model 1,”}\ \ M2=\text{“model 2.”}\n
<table>
<thead>
<tr>
<th>( x )</th>
<th>X in Fe-X</th>
<th>( R/a )</th>
<th>( J_{ij} )</th>
<th>( (J_{ij})_{im} )</th>
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<td>Fe</td>
<td>0.331</td>
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<td>2</td>
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<tr>
<td>( 5.0 )</td>
<td>Fe</td>
<td>0.663</td>
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<td>[0.22,−0.07,1/2]</td>
<td>8</td>
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<tr>
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<td>Fe</td>
<td>0.663</td>
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<tr>
<td>( 6.0 )</td>
<td>Rh</td>
<td>0.282</td>
<td>[0.22,−0.07,1/2]</td>
<td>8</td>
</tr>
<tr>
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<td>Rh</td>
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<td>[0.22,−0.07,1/2]</td>
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<td>Rh</td>
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<td>[0.43,−0.29,1/2]</td>
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</tbody>
</table>

\( \omega_{ij}(k) \) should be constant along any direction in planes perpendicular to the direction of the chain. \( \omega_{ij}(k) \) curves for \( \text{Sc}_2\text{FeRh}_{2}\text{B}_2 \), shown in Fig. 8, were calculated using Eq. (B1) in Appendix B and the theoretical \( J_{ij} \) values from Table II. The strongest dispersions, \( \sim 100 \text{ meV} \), occur along the \( \Gamma-Z \) and \( A-M \) directions, which are parallel to the 1D Fe chains; there are also significant dispersions, \( \sim 25 \text{ meV} \), along both the \( \Gamma-X \) and \( \Gamma-M \) directions, which are perpendicular to these chains. Such dispersion cannot be presented in strictly 1D magnetic systems.
Since there are only two magnetic atoms in the unit cell in and calculated the integral in expression
structure results of the compound with 65 valence electrons 
pound with 62 valence electrons, we used the electronic
presented in states/eV cell, whereas partial DOS curves are presented in states/eV atom.

The other interesting “feature” of the calculated \( \omega_0(\mathbf{k}) \) curves is the existence of an optical mode located around 170 meV. This branch of the magnon spectrum is determined by fast oscillations of the small magnetic moments at Rh2 sites in the field produced by interaction with Fe atoms.

In model 2, all interactions \( J_{ij} \) are localized between Fe sites. The presence of Rh/Ru atoms both enhances Fe-Fe exchange interactions within chains up to 21 and 2 meV and produces sizable interactions (~0.5 meV) between chains. Since there are only two magnetic atoms in the unit cell in model 2, \( \omega_0(\mathbf{k}) \) curves (Fig. 8) have only two branches but the dispersion in directions perpendicular to the Fe chains is significant. This dispersion is determined by exchange couplings \( J_{ij} \) and \( J_{ks} \), which are almost 20 times smaller than intra-chain coupling \( J_{i} \) (see Table II) for Sc2FeRh2B2 (\( x = 1.0 \)). A similarly small in-plane dispersion should be expected in the FM-ordered compound with \( x = 0.8 \). However, for lower values of \( x \) and AFM ordering, these exchange interactions are much larger, and we anticipate larger in-plane dispersion of these magnon waves. Since \( \omega_0(\mathbf{k}) \) are determined by the poles of the dynamic transverse magnetic susceptibility \( \chi^+(\mathbf{k}, \omega) \), to verify the applicability of both approximations, more accurate calculations of \( \omega_0(\mathbf{k}) \) from \( \chi^+(\mathbf{k}, \omega) \) need to be done. For the purpose of estimating the values of the pairwise exchange interactions \( J_{ij} \) in a compound with 62 valence electrons, we used the electronic structure results of the compound with 65 valence electrons and calculated the integral in expression (2) up to an \( E_F \) value that gives the occupation of rigid bands to be 62 electrons. The largest \( J_{ij} \) values (~9 meV in LSDA) calculated by this approach are negative and correspond to interactions between two Fe atoms in the unit cell related to the vector

\( \langle a/2(x+y) \rangle \) (entry 3 in Table II). From this result, a possible ground state for this spin system is AFM with the magnetic moments of the two chains of Fe atoms along the \( c \) direction in the unit cell aligned along opposite directions.

To check the applicability of the rigid-band approximation, we also calculated \( \langle J_{0}/\mu_B \rangle \) as a function of the band energy for Sc2FeRu2B2 and placed it on the same plot with the calculated results of Sc2FeRh2B2 (see again Fig. 7). The two curves show the same general tendencies with qualitative similarities. Any numerical discrepancies are almost exclusively related to the ~20% larger bandwidth of the Ru 4d band compared to the Rh 4d band. This well-known phenomenon, which is readily apparent from the DOS curves of elemental fcc Ru and fcc Rh, but using the lattice parameter for Ru, can be attributed to the larger effective nuclear charge of Rh over Ru and the corresponding greater orbital overlaps between Ru atoms than between Rh atoms.

An impressive example of the influence of Ru/Rh substitution on physical properties occurs in the perovskitelike phases CaRu1−xRhxO3.35 Low doping levels of Rh for Ru into this phase effectively narrows the 4d band and enhances the spin correlation. This effect triggers a metal-insulator transition and alters the spin coupling, thereby giving rise to a magnetically ordered phase. In our Sc2Fe(Ru1−xRh)xB2 case, the substitution of Rh by Ru leads to a significant reduction of the spin moment at the Fe atoms, namely, from 3.42\( \mu_B \) to 2.70\( \mu_B \). For the other magnetically active atoms, the corresponding change is from 0.25\( \mu_B \) at Rh to −0.08\( \mu_B \) at Ru. Such a reduction of the magnetic characteristics siz-

FIG. 5. Total and partial DOS curves in FM Sc2FeRh5B2. The Fermi level corresponds to the energy zero. The total DOS is presented in states/eV cell, whereas partial DOS curves are presented in states/eV atom.

FIG. 6. (Color online) (Top) The effective exchange constant \( (J_{0})_{\mu_B} \) as a function of band filling in Sc2FeRh5B2 (65 valence electrons, in red solid) and in Sc2FeRu5B2 (60 valence electrons, in blue dashed). (Middle and bottom) The partial DOS curves, respectively, for Fe and Ru/Rh sites. The Fermi levels are shown by vertical lines, with the zero energy corresponding to an occupation number of 65 valence electrons.
FIG. 7. (Color online) The effective exchange constant \( J_0 \) as a function of valence electron count \( N \) calculated for \( \text{Sc}_2\text{FeRh}_5\text{B}_2 \) (red solid) and \( \text{Sc}_2\text{FeRu}_5\text{B}_2 \) (blue dashed) assuming a rigid-band approximation for FM (top) and AFM (bottom). Individual points in the top/bottom figures correspond to exact calculated results as a function of \( N \). (Middle) The total energy difference between FM and AFM ordering, \( \Delta E = E_{\text{FM}} - E_{\text{AFM}} \). The green point identifies \( \Delta E \) between the FM and AFM-2 magnetic structures (see text).

The effective exchange constant \( J_0 \) changes from FM to AFM at \( N \approx 63 \) valence electrons, see above) and below (see Fig. 7, middle). This result is independent of both LSDA and GGA approaches. The only exception occurs for \( x = 0.2 \), where AFM ordering is stable for LSDA but FM for the GGA approach. However, we shall demonstrate that AFM ordering is quite complicated at this concentration. Together with the change of the ground-state magnetic ordering with chemical composition, the orientations of the induced magnetic moments at Ru (or Ru) also change their directions, from a parallel to an antiparallel orientation with respect to the Fe atoms (see spin moments in Table I). At \( x = 0.2 \), the effective exchange parameter \( J_0 \) is raised because of a significant compensation of nearest neighbor interactions by the next nearest neighbors (Table II). In such a “frustrated” system, more complicated types of magnetic ordering are likely, such as antiferromagnetism with large or even incommensurate ordering vectors. The classical ground state of the Heisenberg Hamiltonian (1) is known to be of the form \( S_i = u \cos(Q \cdot R_i) + v \sin(Q \cdot R_i) \), where \( u \) and \( v \) are two orthogonal vectors, \( R_i \) is the position of site \( i \) in real space, and the wave vector \( Q \) has to minimize \( J(q) \), which is the Fourier transform of the pairwise exchange parameters, \( J(q) = \sum_{i,j} J_{ij} \cos(q \cdot (R_i - R_j)) \). For the cases of either FM or AFM ordering used to calculate the \( J_{ij} \) values, the wave vector \( Q \) should correspond to zero. As seen from the \( J(q) \) variations along various symmetry directions in the Brillouin zone in Fig. 9, neither FM nor AFM ordering based on one unit cell satisfies this condition. The minima of \( J(q) \) correspond to incommensurate spin structure with a characteristic wave vector \( Q = (2\pi/a) \cdot [0,0,1/4(a/c)] \) and based on an AFM unit cell. This type of magnetic ordering was reproduced in the crystallographic unit cell by four unit cells repeated along the \( c \) direction (AFM-2). The magnetic moments of two Fe atoms in the two bottom cells are aligned in antiparallel directions. In the two top cells, magnetic moments are rotated by \( 180^\circ \). The excess energy of the AFM-2 state as compared to the FM state is shown by the green point in Fig. 7 for \( N = 61 \) valence electrons.

Nonetheless, the ground state for \( \text{Sc}_2\text{FeRu}_5\text{B}_2 \) with \( x = 0 \) is FM ordered, and \( \Delta E \) equals 257 K (47 K in GGA) in favor of antiferromagnetism. In contrast to \( \text{Sc}_2\text{FeRh}_5\text{B}_2 \) with \( x = 1 \), FM ordering is unstable, \( (J_0)_{\text{FM}} < 0 \), while the \( (J_0)_{\text{FM}} \) value in the AFM-ordered phase is positive (17.4 meV in LSDA; 22 meV in GGA model 1, 49 meV in model 2). The Néel
exchange coupling

IV. CONCLUSIONS

For the entire homologous series Sc\textsubscript{2}Fe(Ru\textsubscript{1-x}Rh\textsubscript{x})\textsubscript{3}B\textsubscript{2}, magnetic measurements show a change from FM to AFM behavior as x decreases. The relationship between effective exchange coupling (J\textsubscript{0}), and COHP along the 3d series was investigated on a sample of bcc Fe. This analysis indicated the tendency for AFM ordering for nearly the half-filled band cases (Cr and Mn) and FM ordering for almost empty or almost filled band cases (Fe, Co, and Ni), and that this behavior correlates with the Fermi level falling, respectively, among metal-metal nonbonding or antibonding states. The general character of this trend was demonstrated on a calculation of (J\textsubscript{0}), using a model rectangular DOS. Using the same technique, the effective exchange interactions (J\textsubscript{0}), in Sc\textsubscript{2}Fe(Ru\textsubscript{1-x}Rh\textsubscript{x})\textsubscript{3}B\textsubscript{2} followed a similar trend to 3d bcc metals as composition varies: (J\textsubscript{0}), takes negative values (AFM ordering) for low x with the Fermi level at metal-metal nonbonding states and changes to positive values (FM ordering) as x increases when the Fermi level falls at metal-metal antibonding states. Inclusion of gradient corrections to the local-spin-density approximation leads to larger magnetic moments and exchange interactions, but does not change this dependence. We propose a model in which Fe atomic moments are described by an independent rigid spin whereas interaction with the Rh/Ru magnetic sublattice leads to enhancement of Fe-Fe exchange. This description reproduces the Curie temperatures in much better agreement with experiment. Although transition temperatures are severely underestimated for FM phases and overestimated for AFM by both LSDA- and GGA-based models 1 and 2, the trends in magnetic ordering behavior are very well reproduced. The effective exchange couplings reveal significant Rh-Fe interactions that are the leading contributions to the FM coupling in the Rh-rich samples. In model 2, these interactions produce significant enhancement both within and between Fe chains. According to the calculation of spin wave dispersion, these Rh-Fe interactions eliminate 1D magnetic character for these materials. Furthermore, an incommensurate magnetic ordering along the c direction is predicted for a concentration x=0.2.

ACKNOWLEDGMENTS

One of the authors (G.D.S.) would like to thank N. E. Zein, O. N. Mryasov, and S. Blügel for helpful discussions. The authors acknowledge the generous financial support through a joint grant provided by the U.S. National Science Foundation (NSF DMR 05-02671) and the Deutsche Forschungsgemeinschaft (Germany).

APPENDIX A: CALCULATION OF PAIR AND EFFECTIVE EXCHANGE COUPLINGS

The pairwise exchange parameters J\textsubscript{ij} are obtained by multiple scattering theory according to

\[ J_{ij} = \frac{1}{2\pi} \int_{E_F} dE \text{ Im} \sum_{L,L'} \left[ \delta P_{L'\downarrow}(T^L_{i,i;j,j}T^L_{j,j;i,i}) + T^L_{i,i;j,j}T^L_{j,j;i,i}\delta P_{L'\downarrow}\right]. \]  

TABLE III. Calculated pairwise exchange parameters J\textsubscript{ij} (meV) for Fe-X pairs (index i=Fe), R/a being the relative interatomic distance, [R\textsubscript{1}/a,R\textsubscript{2}/a,R\textsubscript{3}/a,R\textsubscript{4}/a] the corresponding vector, M is the number of equivalent pairs, \(\Delta C=C_i-C_j\) is the splitting between spin up and down 4d states of Rh/Ru atoms, J\textsubscript{aa} is on-site exchange parameter for Rh/Ru, and I\textsubscript{aa} is the renormalized Stoner exchange parameter used for calculation of enhanced Fe-Fe interactions as in Appendix C.

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<th>LDA</th>
<th>GGA</th>
<th>LDA</th>
<th>GGA</th>
<th>(\Delta C)</th>
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<td>-0.04</td>
<td>-0.04</td>
<td>9</td>
<td>-0.03</td>
<td>18</td>
</tr>
</tbody>
</table>
where \( \delta P(e)_{ij} = [P^s_{ij}(e) - P^e_{ij}(e)] / 2 \) is the on-site perturbation at atom \( i \) with orbital moment \( l \), \( P^s_{ij}(e) \) is the potential function for site \( i \) with spin \( \sigma \), \( P^e_{ij}(e) = [1/(2(2l+1))] [D^s_{ij}(e) + l + 1/D^e_{ij}(e)] \), \( D^s_{ij}(e) \) is a wave function logarithmic derivative at the corresponding atomic sphere radius, and \( T^\sigma_{iL,l',L'}(e) \) is the scattering-path operator connecting atoms \( i \) and \( j \), depending on the complex energy \( e \) for the channel with spin \( \sigma \) \( (\uparrow \text{ or } \downarrow) \). \( L \) stands for \((l,m)\), i.e., the orbital moment and its projection.\(^\text{13}\)

The scattering-path operator for the complex energy \( e \) is characterized in terms of the site-diagonal potential function \( P \) and the potential-independent structure constant \( S \),

\[
T^\sigma_{iL,l',L'}(e) = \int \frac{dk}{\Omega_{BZ}} \, e^{i k \mathbf{R}_{ij}} \left( P^s_{ij}(e) - S_{iL,l',L'} \right)^{-1},
\]

where the integral is calculated over the irreducible wedge of the Brillouin zone and \( \mathbf{R}_{ij} \) corresponds to the vector connecting atoms \( i \) and \( j \). Note that \( P(e) \) is parametrized; the parametrization we employ corresponds closely to Anderson’s third-order ASA Hamiltonian

\[
P^{-1}(z) = \frac{\Delta}{C - z'} + \gamma - \alpha,
\]

with

\[
z' = z + p(z - e_v)^3,
\]

where \( C, \Delta, \gamma, p, \) and \( e_v \) are standard LMTO parameters and \( \alpha \) is the screening parameter.\(^\text{37}\) For the calculation of the \( T \) matrix, we use the bare representation, in which the screening parameter \( \alpha = 0 \).

Using the “sum rule,” one may obtain\(^\text{13}\) the expression for the effective ("on-site") exchange parameter to be

\[
(J_0)_{ij} = \sum_l J_{ij} = \frac{1}{2 \pi} \oint_{CF} \, de \, \text{Im} \sum_{L,L'} \left[ \delta P_{iL,L'}(T^s_{ij}) \right]_L \left[ T^\uparrow_{iL,L'} \right]_L - \left[ T^\downarrow_{iL,L'} \right]_L + 2 \delta P_{iL,L'} T^\uparrow_{iL,L'} \delta P_{iL,L'} T^\downarrow_{iL,L'}],
\]

The above energy integrals in Eq. (A1) and (A5) were evaluated using a Gaussian quadrature with 12 points on an ellipse in the complex plane. Both the quadrature procedure and the number of \( k \) points in the Brillouin zone integral were carefully checked for their convergence properties.

**APPENDIX B: EXPRESSION FOR SPIN WAVE DISPERSION IN THE SYSTEM WITH FEW ATOMS IN THE UNIT CELL**

To obtain the magnon dispersion curves in the system with few magnetic atoms in the unit cell, we solved equation of motion for magnetic moments in the linear limit.\(^\text{38}\) The spin wave dispersions, \( \omega_{\nu}(k) \), where \( \nu \) labels each band, are calculated as the eigenvalues of the system of linear equations

\[
\sum_n \left[ 4(J_0)_{n}(0) \delta_{nm} \frac{M_n}{\left| M_n \right|} (\mathbf{J}_n)(k) - \left| M_n \right| \omega_{\nu}(k) \delta_{nm} \right] e_{m}(k, \nu) = 0,
\]

where \( n \) and \( m \) are magnetic sublattices, \( M_n \) is the magnetic moment of atom \( n \) and \( \left| M_n \right| \) is its absolute value, \( \delta_{nm} \) is the Kronecker delta (1 for \( n \neq m \), 0 for \( n = m \)). \( \epsilon_m(k, \nu) \) is the eigenvector, and \( (J_0)_{n}(k) = \sqrt{2/(N \epsilon_n)} \, j_{\epsilon_n} \mathbf{R}_m(k) \) with atom \( i \) from sublattice \( n \), and \((J_0)n(0) = \sum_m M_m / \left| M_m \right| (J_0)_{nm}(k = 0) \). This expression for \( \omega_{\nu}(k) \) is equivalent to the earlier results from the Ref.\(^\text{39}\). In contrast to the expressions from Ref.\(^\text{39}\) however, we include the size of the magnetic moment \((\left| M_n \right|)\) in the definition of \( J_{ij} \).

**APPENDIX C: EXPRESSION FOR RENORMALIZED EXCHANGE COUPLINGS**

Following expression (5) for renormalized Fe-Fe pair exchange parameters, \( J_{ij} \) can be expressed as

\[
\bar{J}_1 = J_1 + 4J_1 \bar{J}_a J_6 + 4J_1 \bar{J}_8 J_7 + 2 \times 4J_6 \bar{J}_a J_8
\]

\[
\bar{J}_2 = J_2 + 2 \times 4J_6 \bar{J}_a J_8
\]

\[
\bar{J}_3 = J_3 + 4J_1 \bar{J}_a J_7
\]

\[
\bar{J}_4 = J_4 + 4J_6 \bar{J}_a J_8
\]

\[
\bar{J}_5 = J_5.
\]

The notation for \( J_1 \) follows Table II; values for \( J_8 \) and \( \bar{J}_a \) are listed in Table III.

The enhanced Rh/Ru Stoner exchange integral \( \bar{J}_a \) was calculated from \( J_a \) (50 mRy) (Ref.\(^\text{27}\)) using the expression

\[
\bar{J}_a = \frac{(4I_a / \Delta C)^2}{1 - (4I_a / \Delta C)^2} J_{aa}.
\]

Finally, the expressions for renormalized effective Fe exchange couplings are

\[
(J_0)_{11} = (J_0)_{11} + 4(J_0)_{13} 4\bar{T}_a (J_0)_{13} 13/8 + 4(J_0)_{11} 4\bar{T}_a (J_0)_{13} 13/8
\]

\[
(J_0)_{12} = (J_0)_{12} + 4(J_0)_{12} 4\bar{T}_a (J_0)_{13} 13/4 + 4(J_0)_{12} 4\bar{T}_a (J_0)_{13} 13/4.
\]

There are two Fe atoms in the unit cell and index "11" corresponds to effective exchange coupling of the first Fe atom with all first atoms in other unit cells and index "12" for the first Fe with all second Fe atoms. The second index corresponds to number of line \( m \) of \((J_0)_{nm}\), as it presented in Table II. The coefficient 1/4 in expression (C3) arises because tabulated values include fourfold degeneracy; 1/8 corresponds to the usual 1/4 factor times an additional 1/2 to exclude self-interactions between Fe moments.
J. van Vleck, Rev. Mod. Phys. 17, 27 (1945).
F. Bloch, Z. Phys. 61, 206 (1930).