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The exchange interaction parameters of Gd monopnictides are deduced from fitting the total energies of different magnetic configurations to those computed within the Heisenberg model. The magnetic structures predicted by first-principles calculations as well as the Curie (Néel) temperatures obtained from Monte Carlo simulations are both in good agreement with experiments. A detailed analysis of the exchange parameters suggests that the Ruderman-Kittel-Kasuya-Yosida-type indirect exchange interactions and antiferromagnetic superexchange interactions coexist in these compounds. The magnetic order changes from ferromagnetic in GdN to antiferromagnetic in other Gd pnictides as a result of the increased ionic radius of a pnictide in the latter. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2200767]

Magnetic ordering of the rare-earth pnictides RX (R is a rare-earth element and $X=$ N, P, As, Sb, Bi) has long been of interest because of their "coupled" magnetic and electronic properties.[1–14] This interest is enhanced by the wide industrial applications of the rare-earth pnictides[15] with possible use as spin filters and robust magnetoresistive materials for spintronics.[16]

Even after more than 40 years efforts,[1–14] a thorough understanding of the magnetic ordering of RX compounds, with simple NaCl-type structure, is still elusive. The persistent difficulty is finding an accurate description of the highly localized open shell $4f$ electrons, which is a key to understanding the magnetic properties and other fascinating many-body characteristic of the rare earths and rare-earth compounds. The $4f$ electrons are well localized and the direct $4f$-$4f$ exchange is negligible. Thus, in the rare-earth metals, the coupling between neighboring magnetic ions occurs through an indirect magnetic exchange of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type.[17] The situation in the RX system is much more complicated. The presence of the pnictide greatly decreases the free charge carrier density and introduces more complicated exchange mechanisms such as superexchange interactions.[18] In addition, in the face-centered cubic (fcc) structure, the two nearest neighboring (NN) atoms of a given atom can themselves be NN atoms, which often causes spin frustration. The combination of all the factors that contribute to the magnetic ordering in rare-earth pnictides renders the problem extremely complex. This complexity is, however, reduced in gadolinium pnictides, where the Gdf orbitals are half occupied, hence the orbital angular momentum is zero. Consequently, the anisotropic and multipole effects are small, thus making the analysis of the magnetic exchange interactions in GdX compounds less demanding.

In a recent letter,[19] we have predicted that the electronic and magnetic properties of GdN are extremely sensitive to the strain effect, resulting in a transformation of this compound from half-metallic to semimetallic and then ultimately to semiconducting with the lattice expansion. In this letter, using first-principles total energy calculations, we present a systematic theoretical study of the magnetic exchange interactions on the whole Gd monopnictide family, GdX ($X=$N, P, As, Sb, Bi). Following description of Ref. 20, we consider four different magnetic ordering configurations: ferromagnetic (FM) and three antiferromagnetic (AFM). The latter are shown in Fig. 1 and denoted by AFM-I, AFM-II, and AFM-III. We predict that the GdX magnetic structure changes from FM in GdN to AFM-II in other GdX compounds in agreement with experimental observations. We demonstrate that this behavior is caused by the coexistence of the RKKY-type indirect exchange interactions and superexchange interactions, the relative contribution of which changes with the ionic radius of pnictides.

Our first-principles calculations are based on density functional theory implemented within the full-potential linear-augmented-plane-wave method.[21] We use a local spin density approximation (LSDA) with additional Hubbard correlation terms U and J associated with the $4f$ narrow bands (the so called LSDA+U approach).[22] Following the previous work,[19] we assume that $U=6.7$ eV and $J=0.7$ eV. Since the energy difference between different magnetic ordering states is small (of the order of a few meV), we use 4000 k points in
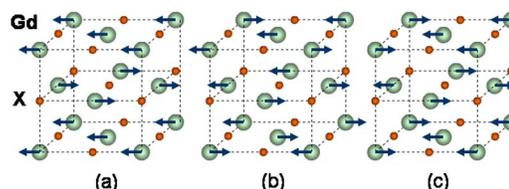

FIG. 1. (Color online) Three antiferromagnetic ordering configurations in Gd pnictides: (a) AFM-I, (b) AFM-II, and (c) AFM-III. The arrows indicate magnetic moment orientations on Gd atoms.

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TABLE I. Calculated total energy differences per formula between ferromagnetic and three antiferromagnetic configurations for Gd monopnictides ΔE_n $=E_n-E_{FM}$ ($n=$I,II,III). The exchange parameters, J_1, J_2, and J_3 are obtained according to Eq. (2). Values inside the parentheses are calculated using the theoretical lattice constants. Theoretical and experimental transition temperatures (Ref. 14) are listed for comparison.

	a(Å) Expt. (Theor.)	ΔE_{I} (meV)	ΔE_{II} (meV)	ΔE_{III} (meV)	J_1 (meV)	J_2 (meV)	J_3 (meV)	$T_{N(C)}$ (K) MC	$T_{N(C)}$ (K) Expt.
GdN	4.97(4.92)	6.7(7.1)	4.2(5.1)	6.5(7.3)	0.86(0.95)	−0.14(−0.04)	−0.01(−0.03)	34(38)	58.0
GdP	5.71(5.63)	−2.8(−3.3)	−6.5(−6.9)	−3.5(−4.0)	−0.17(−0.21)	−0.74(−0.74)	−0.09(−0.11)	12(13)	15.9
GdAs	5.86(5.77)	−3.9(−4.3)	−8.4(−8.8)	−4.7(−5.4)	−0.22(−0.34)	−0.91(−0.93)	−0.13(−0.10)	14(16)	18.7
GdSb	6.22(6.11)	−5.7(−6.6)	−11.1(−11.5)	−7.2(−7.9)	−0.51(−0.60)	−1.13(−1.10)	−0.10(−0.11)	20(19)	23.4
GdBi	6.30(6.24)	−6.9(−7.3)	−13.4(−13.8)	−8.8(−9.3)	−0.66(−0.71)	−1.37(−1.38)	−0.10(−0.10)	22(23)	25.8

the Brillouin zone to obtain the total energy accuracy of 0.1 meV.

Our basic strategy is to first deduce the exchange interaction parameters of GdX compounds by fitting the first-principles total energies of different magnetic configurations to those computed within the Heisenberg model,

$$H = -\sum_{n=1,2,3}^{n\text{th NN}} J_n \sum_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j. \qquad (1)$$

Here $\mathbf{S}_i$ is the unit vector in the direction of the magnetic moment at the ith lattice site, J_n is the exchange parameter between the nth NN magnetic atoms, and we limit our consideration to third NN interactions. In this case the difference between the energy of the three AFM states E_n ($n=$I,II,III) shown in Fig. 1 and the energy of the FM state E_{FM} are

$$\Delta E_{\mathrm{I}} \equiv E_{\mathrm{I}} - E_{FM} = 8J_1 + 16J_3,$$

$$\Delta E_{\mathrm{II}} \equiv E_{\mathrm{II}} - E_{FM} = 6J_1 + 6J_2 + 12J_3, \qquad (2)$$

$$\Delta E_{\mathrm{III}} \equiv E_{\mathrm{III}} - E_{FM} = 8J_1 + 2J_2 + 8J_3.$$

The calculated total energy differences ΔE_n and the resulting exchange parameters, for both experimental and theoretical lattice constants, are listed in Table I. The most important result, evident from Table I, is that our calculations predict correctly the switching from FM ordering of GdN to AFM ordering in the other gadolinium pnictides, GdP, GdAs, GdSb, and GdBi. Moreover, we find that in all these compounds, the total energies of three AFM configurations have a consistent order, i.e., $E_{\mathrm{II}} < E_{\mathrm{III}} < E_{\mathrm{I}}$. This agrees with the experimental observations that all the AFM compounds studied here have the AFM-II structure.[14] Table I also shows that, except J_1 for GdN, all the exchange parameters have negative values, indicating that the exchange interactions in these compounds are antiferromagnetic. With the increase of anion size, as X changes from N to Bi, both J_1 and J_2 decrease rapidly, while the absolute change of J_3 is quite small.

To understand the nature of the exchange interactions in the Gd pnictides, we calculated the dependence of the exchange parameters on the lattice strain. As is evident from Fig. 2, for all the GdX compounds, the absolute value of J_1 increases with the decrease of the lattice constant. This behavior is the signature of the RKKY-type indirect exchange interaction. Indeed, the RKKY-type coupling varies sensitively with the density of charge carriers. The enhancement of the exchange coupling between first NN magnetic sites, when the lattice constant decreases, is caused by the increased number of free charge carriers as the GdX compound becomes more metallic. On the contrary, the J_2 is weakly

dependent on the lattice strain for all the Gd pnictides, except GdN where it decreases appreciably with the increase of the lattice constant. As was explained in Ref. 19, this behavior signifies the strengthening of the AFM superexchange interaction when the system becomes less metallic.

To obtain a more insight into the strength of the superexchange interaction contributing to J_2 we use a model for charge-transfer-type superexchange developed for transition-metal oxides in Ref. 23. Since the induced d moment on Gd (n_d) due to atomic 4f-5d exchange interactions is a small fraction of μ_B compared with an integral value in transition-metal oxides, we scale the superexchange formula in Ref. 23 with n_d. The value of n_d is estimated by subtracting the ideal Gd^{3+} spin moment, i.e., 7, from the calculated total spin moment on Gd ions. Thus an expression for the superexchange interaction takes the form

$$J_2^{\text{super}} = -n_d \frac{t_{pd}^4}{\Delta^3}, \qquad (3)$$

where Δ is the energy difference between the Gd 5d orbital and the outmost p state of X ion and the hopping parameter t_{pd} can be evaluated according to Harrison.[24] Table II shows the so calculated J_2^{super} of the GdX compounds at their experimental lattice constants, together with the corresponding values of t_{pd}, Δ, n_d, Gd ion magnetic moment μ_{Gd}, anion size R_X, and interatomic distance R_{ij} used in the calculation. We see from Table II that our qualitative estimate of J_2^{super} is of the order of J_2 for all the GdX compounds. Thus, the second NN exchange parameters seem to be primarily due to the superexchange interaction. GdN may be the only exclusion from this rule—the decrease of J_2 versus lattice strain indicates the weakening of the indirect exchange coupling.[19]
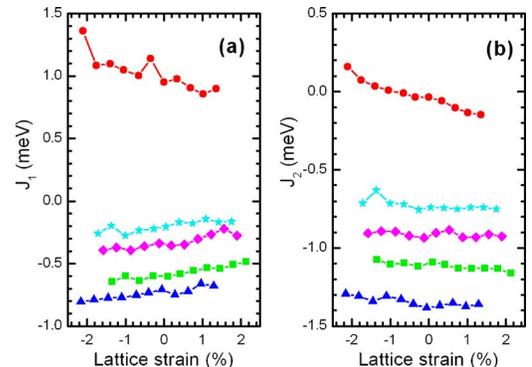

FIG. 2. (Color online) Calculated exchange parameters J_1 (a) and J_2 (b) for Gd pnictides as a function of the lattice strain: GdN (circles), GdP (stars), GdAs (diamonds), GdSb (squares), and GdBi (triangles). The lattice strain is defined by the relative deviation of the lattice constant from the theoretical equilibrium lattice constant.

TABLE II. Estimated superexchange energies J_2^{super} between the second nearest neighboring Gd ions on the experimental structures of GdX and parameters used for this estimate: the anion size R_X, the interatomic distance R_{ij}, Gd ion magnetic moment μ_{Gd}, the occupation number n_d of the d orbital, the hopping parameter t_{pd}, and the energy difference Δ between the Gd $5d$ orbital, and the outmost p state of X ion. The radius of Gd $5d$ orbital is 1.78 Å.

	R_X (Å)	R_{ij} (Å)	μ_{Gd} (μ_B)	n_d	t_{pd} (eV)	Δ (eV)	J_2^{super} (meV)
GdN	0.70	2.48	7.038	0.038	0.754	3.4	−0.31
GdP	1.07	2.85	7.068	0.068	0.637	2.5	−0.72
GdAs	1.15	2.93	7.076	0.076	0.611	2.4	−0.77
GdSb	1.33	3.11	7.096	0.096	0.552	2.1	−0.96
GdBi	1.37	3.15	7.104	0.104	0.540	2.0	−1.11

Using Monte Carlo (MC) simulations based on the Heisenberg Hamiltonian (1) and the first-principles exchange parameters we calculated the transition temperatures of the GdX compounds (the Curie temperature T_C for GdN and the Néel temperatures T_N for the other Gd pnictides). In the MC simulations we used a $10a \times 10a \times 10a$ supercell (which includes 4000 spins) with periodic boundary conditions (here a is the lattice constant). As is evident from Table I, our MC simulations not only accurately reproduce the experimentally observed ground states for these five compounds but also predict the transition temperatures in good agreement with experiments. Given the strong correlated nature of the Gd pnictides, this agreement is quite impressive, supporting the validity of our first-principles results.

Following the above analysis, a whole picture on the magnetic coupling in GdX systems can be described as follows. As we know, Gd metal with hcp structure is ferromagnetic at room temperature ($T_C = 293.2$ K).[25] The NN distance of bulk Gd at the experimental lattice constant is 3.63 Å. This spacing of magnetic moments is just slightly larger than that of GdN (3.51 Å). Since hcp and fcc structures have exactly the same number of the first and second NN atoms, it is not surprising that, similar to Gd metal, the J_1 exchange in GdN is ferromagnetic; just the value of $J_1 = 0.86$ meV in GdN is much smaller than $J_1 \approx 7.0$ meV in Gd metal, due to GdN's poor metallicity. The superexchange contributions in GdN are not strong enough to offset those contributions from the RKKY-type ferromagnetic interactions. Thus GdN is ferromagnetic with a low transition temperature (58 K). With the increase of anion size, the superexchange is strengthened causing the J_2 parameter to decrease. In addition, the J_1 exchange also becomes antiferromagnetic. The variation of J_1 as a function of the lattice strain indicates that this variation is caused by the RKKY-type indirect exchange interaction. However, we do not exclude the possibility of the contribution from the 90°-superexchange interaction that can be quite large in some oxides.[26] Generally speaking the overall effect, after the competition between the various magnetic interactions is taken into account, is that antiferromagnetic ordering gains the upper hand, though the Néel temperature is rather small, but the antiferromagnetic ordering increases with the pnictide anion size.

Based on the predicted interplay between the exchange coupling, the pnictide anion size, and the lattice constant, we suggest that there likely exist gadolinium compounds in which both J_1 and J_2 are ferromagnetic. Such materials might have larger effective exchange coupling and higher transition temperature than those of the simple stoichiometric rare-earth compounds. An example of this is the higher T_C obtained by doping GdN with carbon.[27]

In summary, we find that there are profound changes in the magnetic ordering behavior between pure Gd, GdN, and GdP. Density functional theory with the Hubbard correlation terms gives an adequate description of the magnetic properties of Gd monopnictides. We have been able to deduce the exchange parameters of these systems directly from *ab initio* calculations and to verify them by MC simulations. The magnetic orderings of Gd monopnictides are determined by the interplay between the first and second NN exchange interactions. Our results clearly demonstrate the coexistence of the RKKY-type magnetic interaction and the superexchange interaction, the relative contribution of which changes with the ionic radius of pnictides.

[1] H. R. Child, M. K. Wilkinson, J. W. Cable, W. C. Koehler, and E. O. Wollan, Phys. Rev. **131**, 922 (1963).
[2] G. T. Trammell, Phys. Rev. **131**, 932 (1963).
[3] A. Hasegawa and A. Yanase, J. Phys. Soc. Jpn. **42**, 492 (1977).
[4] R. Monnier, J. Rhyner, T. M. Rice, and D. D. Koelling, Phys. Rev. B **31**, 5554 (1985).
[5] G. Travaglini, F. Marabelli, R. Monnier, E. Kaldis, and P. Wachter, Phys. Rev. B **34**, 3876 (1986).
[6] J.-B. Xia, S.-F. Ren, and Y.-C. Chang, Phys. Rev. B **43**, 1692 (1991).
[7] A. I. Liechtenstein, V. P. Antropov, and B. N. Harmon, Phys. Rev. B **49**, 10770 (1994).
[8] A. G. Petukhov, W. R. L. Lambrecht, and B. Segall, Phys. Rev. B **53**, 3646 (1996).
[9] W. R. L. Lambrecht, B. Segall, A. G. Petukhov, R. Bogaerts, and F. Herlach, Phys. Rev. B **55**, 9239 (1997).
[10] C. Stampfl, W. Mannstadt, R. Asahi, and A. J. Freeman, Phys. Rev. B **63**, 155106 (2001).
[11] Chun-Gang Duan, R. F. Sabiryanov, Jianjun Liu, W. N. Mei, P. A. Dowben, and J. R. Hardy, J. Appl. Phys. **97**, 10A915 (2005).
[12] S. J. Allen, Jr., N. Tabatabaie, C. J. Palmstrøm, G. W. Hull, T. Sands, F. DeRosa, H. L. Gilchrist, and K. C. Garrison, Phys. Rev. Lett. **62**, 2309 (1989).
[13] T. Chattopadhyay, P. Burlet, J. Rossat-Mignod, H. Bartholin, C. Vettier, and O. Vogt, Phys. Rev. B **49**, 15096 (1994).
[14] D. X. Li, Y. Haga, H. Shida, T. Suzuki, Y. S. Kwon, and G. Kido, J. Phys.: Condens. Matter **9**, 10777 (1997).
[15] For a complete review, see the series *Handbook on Physics and Chemistry of Rare Earth* (North-Holland, Amsterdam, 1979).
[16] D. E. Brehmer, K. Zhang, C. J. Schwarz, S. P. Chau, and S. J. Allen, Appl. Phys. Lett. **67**, 1268 (1995).
[17] Ph. Kurz, G. Bihlmayer, and S. Blügel, J. Phys.: Condens. Matter **14**, 6353 (2002).
[18] P. W. Anderson, Phys. Rev. **79**, 350 (1950); **115**, 2 (1959).
[19] Chun-Gang Duan, R. F. Sabiryanov, Jianjun Liu, W. N. Mei, P. A. Dowben, and J. R. Hardy, Phys. Rev. Lett. **94**, 237201 (2005).
[20] J. Samuel Smart, *Effective Field Theories of Magnetism* (Saunders, Philadelphia, 1966), pp. 76–77.
[21] K. Schwarz, P. Blaha, and G. K. H. Madsen, Comput. Phys. Commun. **147**, 71 (2002).
[22] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).
[23] V. A. Gubanov, A. V. Postnikov, and A. I. Likhtenshtein, *Magnetism and the Electronic Structure of Crystals* (Springer, New York, 1992), p. 23.
[24] W. A. Harrison, *Electronic Structure and The Properties of Solids* (Freeman, San Francisco, 1980), pp. 451, 481, and 505.
[25] H. E. Nigh, S. Legvold, and F. H. Spedding, Phys. Rev. **132**, 1092 (1963).
[26] W. Geertsma and D. Khomskii, Phys. Rev. B **54**, 3011 (1996).
[27] M. Kuznietz, J. Appl. Phys. **42**, 1470 (1971).