Anisotropic exchange coupling in diluted magnetic semiconductors: *Ab initio* spin-density functional theory

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A different scheme to calculate the exchange tensor $\underline{\underline{J}}_{ij}$ describing in a phenomenological way the anisotropic exchange coupling of two moments in a magnetically ordered system is presented. The *ab initio* approach is based on spin-polarized relativistic multiple-scattering theory within the framework of spin-density functional theory. The scheme is applied to ferromagnetic CrTe as well as the diluted magnetic semiconductor system $Ga_{1-x}Mn_xAs$. In the latter case the results show that there is a noticeable anisotropy in the exchange coupling present, although not as pronounced as those suggested in recent theoretical investigations.

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I. INTRODUCTION

The mapping of the energy of a magnetic solid calculated from first principles for different magnetic configurations onto a Heisenberg Hamiltonian is nowadays a widely used concept that allows a number of interesting subsequent investigations. An example of this is the determination of the Curie temperature of a ferromagnet by means of Monte Carlo simulations using the calculated exchange coupling parameters J_{ij} as input (i and j are indices labeling the individual atomic sites).[1] Apart from fitting the J_{ij}'s to the total energies obtained for different magnetic configurations, one can use the energies of spin spirals as basis for such mapping.[2] As an alternative one may use perturbation theory that allows the calculation of the J_{ij}'s directly. In fact the expression derived by Liechtenstein *et al.*[3] within the frame work of nonrelativistic multiple-scattering theory is now successfully used for a wide range of materials.[4–6]

Initiated among others by investigations on the magnetic ground-state configuration of nanoscale systems, there is strongly growing interest in the interplay of exchange coupling and spin-orbit coupling (SOC).[7] Besides the magnetic anisotropy energy, the spin-orbit coupling gives rise to an anisotropic exchange coupling. Using again the above mentioned concept the isotropic exchange constants J_{ij} have to be replaced by a corresponding exchange coupling tensor $\underline{\underline{J}}_{ij}$. By generalizing the approach of Liechtenstein *et al.*[3] to a fully relativistic formulation, Udvardi *et al.*[8] derived corresponding expressions for the elements of $\underline{\underline{J}}_{ij}$. Corresponding applications to thin films as well as to finite deposited clusters can be found in the literature.[8,9] A disadvantage of the expressions worked out by Udvardi *et al.*[8] is that one has to use various magnetic configurations as a reference state to determine all elements of $\underline{\underline{J}}_{ij}$. In the following we present an alternative approach that can be derived in a rather transparent way and does not have that problem. As demonstrated both approaches give nevertheless results that are quite close to each other. As an application of our present scheme we present results for the exchange tensor $\underline{\underline{J}}_{ij}$ in ferromagnetic CrTe and in the diluted magnetic semiconductor (DMS) system $Ga_{1-x}Mn_xAs$. The latter will be discussed in relation to the recent work of Timm and MacDonald,[10] who used a tight-binding description of the system in contrast to the *ab initio* approach employed here that is based on local spin-density approximation (LSDA).

II. THEORETICAL APPROACH

The starting point of our derivation for $\underline{\underline{J}}_{ij}$ is the expression for the change in energy ΔE_{ij} of a system with a perturbation taking place at sites i and j. An expression for ΔE_{ij} was worked out by several authors[3,11] within the framework of multiple-scattering theory and by making use of Lloyd's formula. The derivation of this expression can straightforwardly be applied when working in the framework of spin-polarized relativistic (SPR) multiple scattering or Korringa-Kohn-Rostoker (KKR) (Ref. 12) formalism. Adopting the convention for the corresponding electronic Green's function as used by Dederichs *et al.*,[13] its off-site part is given by

$$G(\vec{r}_i,\vec{r}_j,E) = -ip\sum_{\Lambda\Lambda'} R^i_{\Lambda}(\vec{r}_i,E)G^{ij}_{\Lambda\Lambda'}(E)R^{j\times}_{\Lambda'}(\vec{r}_j,E), \qquad (1)$$

where $G^{ij}_{\Lambda\Lambda'}(E)$ is the so-called structural Green's function, R^i_{Λ} is a regular solution to the single-site Dirac equation labeled by the combined quantum numbers Λ [$\Lambda=(\kappa,\mu)$], with κ and μ as the spin-orbit and magnetic quantum numbers,[14] and p is the electron momentum. The energy change ΔE_{ij} can then be written as[3,11]

$$\Delta E_{ij} = -\frac{1}{\pi}\Im\int dE\ \mathrm{Tr}\ \Delta\underline{t}^i\underline{G}^{ij}\Delta\underline{t}^j\underline{G}^{ji}, \qquad (2)$$

where $\Delta\underline{t}^i$ is the change in the single-site t matrix due to the perturbation $\Delta V^i(\vec{r})$ at site i and the underline denotes matrices with respect to the quantum numbers Λ. To the first order in $\Delta V^i(\vec{r})$ the change $\Delta\underline{t}^i$ is given by

$$\Delta t^i_{\Lambda'\Lambda} = \int d^3r R^{i\times}_{\Lambda'}(\vec{r})\Delta V(\vec{r})R^i_{\Lambda}(\vec{r}) = \Delta V^{(R)i}_{\Lambda'\Lambda}. \qquad (3)$$

Using instead the convention for the Green's function as used by Györffy and co-workers (see Ref. 15), one may express ΔE_{ij} in terms of the scattering path operator $\tau^{ij}_{\Lambda'\Lambda}(E)$,

$$\Delta E_{ij} = -\frac{1}{\pi}\Im \int dE \ \mathrm{Tr}\ \Delta \underline{V}^{(Z)i} \underline{\tau}^{ij} \Delta \underline{V}^{(Z)j} \underline{\tau}^{ji}, \tag{4}$$

where use have been made of the relation $\underline{G}^{ij} = (\underline{\tau}^{i})^{-1} \underline{\tau}^{ij} (\underline{t}^{j})^{-1}$ for $i \neq j$ and the matrix elements $\Delta V^{(Z)i}_{\Lambda\Lambda'}$ are to be evaluated using the alternative set of regular solutions Z^{i}_{Λ} to the single-site Dirac equation.[12,15]

Changing the orientation of the spin magnetic moment $\vec{m}_i$ within an atomic cell i and adopting the rigid spin approximation (RSA) (Ref. 16) imply a corresponding change in the spin-dependent potential $\beta\vec{\sigma}\vec{B}(\vec{r})$ by

$$\Delta V(\vec{r}) = V_{\hat{n}}(\vec{r}) - V_{\hat{n}_0}(\vec{r}) = \beta\vec{\sigma}(\hat{n} - \hat{n}_0) B(\vec{r}), \tag{5}$$

where β is one of the standard Dirac matrices and $\vec{\sigma}$ is the vector of 4×4-spin matrices.[16] In writing Eq. (5) a collinear spin magnetization within the cell has been assumed together with a change in its orientation from $\hat{n}_0$ to $\hat{n}$. Accordingly, $B(\vec{r})$ corresponds to the difference in the spin-projected potential functions $B(\vec{r}) = \frac{1}{2}[V^{\uparrow}(\vec{r}) - V^{\downarrow}(\vec{r})]$.[12] This leads for the matrix elements $\Delta V^{(Z)i}_{\Lambda\Lambda'}$ to

$$\Delta V^{(Z)i}_{\Lambda\Lambda'} = \sum_{\alpha=x,y,z} \Delta V^{(Z)i\alpha}_{\Lambda\Lambda'} \Delta\alpha \tag{6}$$

with

$$\Delta V^{(Z)i\alpha}_{\Lambda\Lambda'} = \int d^3 r Z^{\times}_{\Lambda}(\vec{r}) \beta\sigma_{\alpha} B(r) Z_{\Lambda'}(\vec{r}). \tag{7}$$

Comparison with the generalized Heisenberg Hamiltonian

$$H_{\mathrm{ex}} = -\frac{1}{2}\sum_{i,j} \hat{e}_i \underline{\underline{J}}_{ij} \hat{e}_j \tag{8}$$

with $\hat{e}_{i(j)}$ as the orientation of the spin magnetic moment at site $i(j)$ allows one to write for the elements of the exchange coupling tensor $\underline{\underline{J}}_{ij}$

$$J^{\alpha_i\alpha_j}_{ij} = -\frac{1}{\pi}\Im \int dE \ \mathrm{Tr}\ \Delta \underline{V}^{(Z)\alpha_i} \underline{\tau}^{ij} \Delta \underline{V}^{(Z)\alpha_j} \underline{\tau}^{ji}. \tag{9}$$

The scheme outlined above has been implemented using the SPR version of multiple-scattering theory.[12,15] All calculations have been done within the framework of the LSDA to spin-density functional theory.[17] To represent the results for the exchange tensor $\underline{\underline{J}}_{ij}$ we use the conventional decomposition of the corresponding Heisenberg Hamiltonian in Eq. (8),[8]

$$H_{\mathrm{ex}} = -\frac{1}{2}\sum_{ij} \hat{e}_i J_{ij} \hat{e}_j - \frac{1}{2}\sum_{ij} \hat{e}_i \underline{\underline{J}}^{S}_{ij} \hat{e}_j - \frac{1}{2}\sum_{ij} \vec{D}_{ij}[\hat{e}_i \times \hat{e}_j]. \tag{10}$$

Here J_{ij} is the isotropic exchange coupling constant, $\underline{\underline{J}}^{S}_{ij}$ is the traceless symmetric part of $\underline{\underline{J}}_{ij}$, and the antisymmetric part is represented by the Dzyaloshinski-Moriya (DM) vector $\vec{D}_{ij}$. It should be emphasized that isotropic in the context of J_{ij} refers to spin space and does not imply that there in no anisotropy in real space, i.e., J_{ij} will in general not only depend on the distance $|\vec{R}_{ij}|$ between two sites but also on the orientation $\hat{R}_{ij}$ of the distance vector.

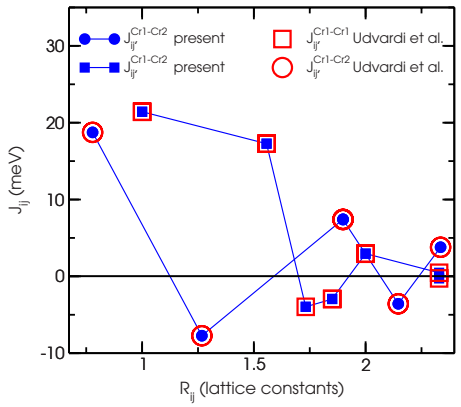

FIG. 1. (Color online) Isotropic exchange interaction parameters J_{ij} between Cr atoms at sites i and j in ferromagnetic CrTe as a function of the interatomic distance R_{ij}. The results based on the present approach (full symbols) are compared to the results obtained using the approach of Udvardi *et al.* (Ref. 8) (open symbols). Circles and squares represent the coupling of a Cr atom in layer 1 (Cr1) to another Cr atom in layer 1 (Cr1) or layer 2 (Cr2), respectively.

III. RESULTS AND DISCUSSION

To demonstrate the application of our approach we present in Figs. 1 and 2 the results for the coupling parameters J_{ij} and $\vec{D}_{ij}$ of the two inequivalent Cr atoms in ferromagnetic CrTe having the NiAs structure. The isotropic parameters J_{ij} shown in Fig. 1 reflect dominating ferromagnetic coupling that is quite far reaching, i.e., slowly decaying. As one notes, the isotropic exchange coupling between a central Cr atom in layer 1 (denoted by Cr1) and another Cr atom in layers 1 and 2 (denoted by Cr1 and Cr2 and represented by squares and circles, respectively, in Fig. 1) is in the same order of magnitude. This means that there is no remarkable spatial anisotropy imposed by the layered structure of the system for the isotropic coupling constant J_{ij}. The anisotropy of the exchange coupling is represented by $\underline{\underline{J}}^{S}_{ij}$ as well as by $\vec{D}_{ij}$. As $\underline{\underline{J}}^{S}_{ij}$ turns out to be quite small we show in Fig. 2 only the three components of the DM vector $\vec{D}_{ij}$. Many of the DM vector components are zero due to symmetry restrictions.[18] In particular one finds a nonzero DM vector $\vec{D}_{ij}$ only if the sites i and j belong to different sublattices Cr1 and Cr2. The different behavior of the x, y, and z components is determined by the lattice symmetry and reflects obviously to some extent the quasilayered structure of the system (hexagonal Cr layers with Te layers in between). However, the anisotropic exchange coupling is still about 2 orders of magnitude smaller than the isotropic one.

As the comparison of the results for J_{ij} and $\vec{D}_{ij}$ obtained using the approach presented above and that of Udvardi *et al.*[8] (in Figs. 1 and 2, respectively) demonstrates, both schemes give very similar results. This also holds for other systems studied so far with most pronounced differences oc-

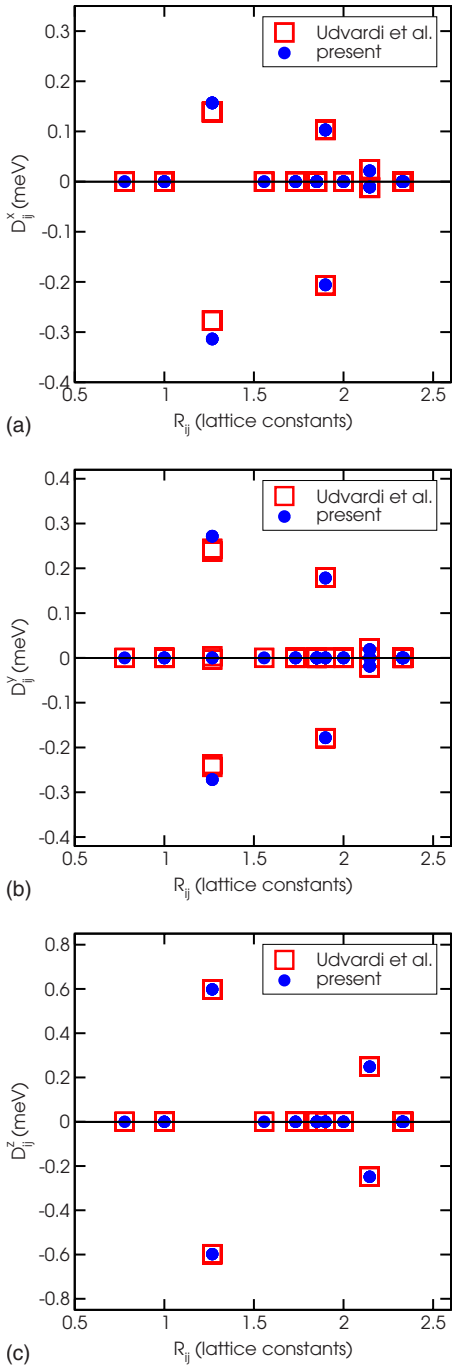

FIG. 2. (Color online) Components of the Dzyaloshinski-Moriya interaction vector $\vec{D}_{ij}$ (from top to bottom: x,y,z) between Cr atoms at sites i and j in ferromagnetic CrTe as a function of the interatomic distance R_{ij}. The results based on the present approach (full circles) are compared to the results obtained using the approach of Udvardi *et al.* (Ref. 8) (open squares).

curring for the DM vector. It should be stressed, however, that the above scheme allows one to determine $\underline{J}_{ij}$ with respect to one common reference state, i.e., there is no need to use various reference states to get all tensor elements. This ensures that the results for the various elements are always consistent even when the choice of the reference state influences the result, e.g., when the RSA is not fully justified.

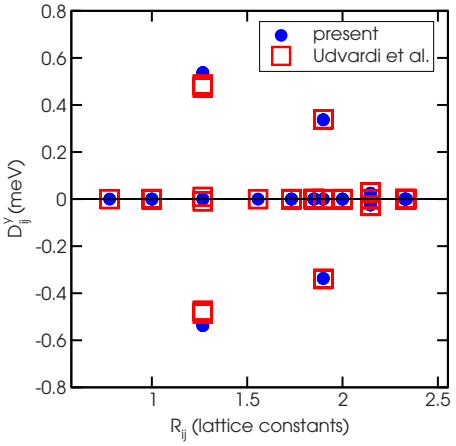

FIG. 3. (Color online) The same as in Fig. 2 middle but with spin-orbit coupling scaled by a factor 2.

To demonstrate that the DM interaction is indeed induced by SOC we performed model calculations with the strength of SOC artificially increased by a factor of 2. While the isotropic exchange coupling constants J_{ij} hardly changed, the DM vector components increased essentially by the same factor. This can be seen by comparing D_{ij}^y (given in Fig. 3) with the results in Fig. 2 (middle).

Figures 4 and 5 show the results of an application of our approach to the diluted magnetic semiconductor system $Ga_{1-x}Mn_xAs$. The Mn atoms were assumed to replace substitutionally the Ga atoms in a random way. The disorder on the Ga sublattice was accounted for by means of the coherent potential approximation (CPA) alloy theory.[4–6] The isotropic exchange coupling (Fig. 4) and also its concentration dependence agree quite well with the results of other authors,[6] indicating in particular that the spin-orbit coupling accounted within the present work affects the isotropic exchange coupling only slightly. As mentioned above and as was noted by other authors[6,19] there is a directional dependency for J_{ij}. This is demonstrated in Fig. 6 where results for the concen-

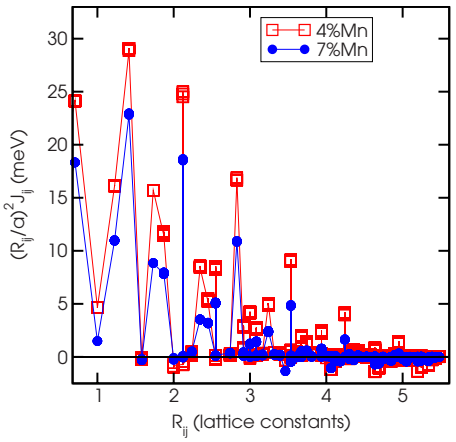

FIG. 4. (Color online) Isotropic exchange interaction J_{ij} between Mn atoms at sites i and j in $Ga_{1-x}Mn_xAs$, scaled by the factor $(R_{ij}/a)^2$, as a function of the interatomic distance R_{ij}. Results are given for 7 at. % Mn (full circles) and for 4 at. % Mn (open squares).

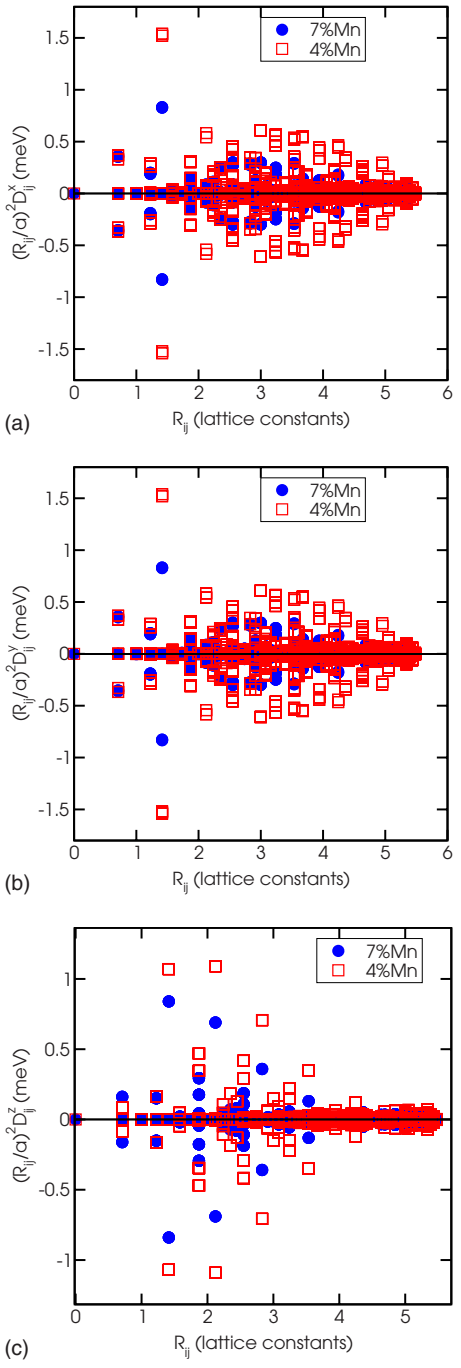

FIG. 5. (Color online) Components of Dzyaloshinski-Moriya interaction vector $\vec{D}_{ij}$ (from top to bottom: x,y,z) between Mn atoms at sites i and j in $Ga_{1-x}Mn_xAs$, scaled by the factor $(R_{ij}/a)^2$, as a function of the interatomic distance R_{ij}. Results are given for 7 at. % Mn (full circles) and for 4 at. % Mn (open squares).

tration $x=0.04$ are given for $\hat{R}_{ij}$ along [001], [110], and [111] separately. As for the magnitude of J_{ij}, this spatial anisotropy of J_{ij} is only slightly influenced by inclusion of SOC. In contrast to this SOC is ultimately responsible for the anisotropy in the exchange coupling represented by the DM vector shown in Fig. 5. (As for CrTe, the symmetric part of $\underline{J}_{ij}$ —symmetric term in Eq. (10)—can again be neglected.) All three components of the DM vectors are of the same order of magnitude as a consequence of the zinc-blende structure of $Ga_{1-x}Mn_xAs$.

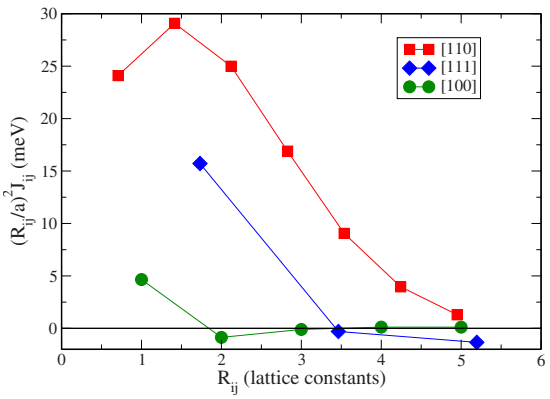

FIG. 6. (Color online) Scaled exchange interactions $(R_{ij}/a)^2 J_{ij}$ in ferromagnetic $Ga_{1-x}Mn_xAs$, where $x=0.04$, as a function of the interatomic distance R_{ij} along different directions.

Although it seems not possible to give a simple scaling behavior of the magnitude of the exchange coupling parameters with respect to the interatomic distance R_{ij}, one notes that the components of $\vec{D}_{ij}$ decay less rapidly as J_{ij} with increasing R_{ij}. This behavior was also found for other systems and is in line with the findings of Timm and MacDonald.[10] However, it should be pointed out that these authors explicitly assumed that a Ruderman-Kittel-Kasuya-Yosida (RKKY)-type mechanism gives rise to the exchange coupling. In fact it has been doubted whether the assumption of RKKY-type coupling as adequate for DMS systems[20] and other mechanisms as double exchange has been discussed.[21] In contrast to the mentioned previous work, no specific coupling mechanism is assumed *a priori* but the exchange coupling tensor is derived directly from the change in energy with a change in the orientation of the magnetic moments. In fact, our results for the isotropic as well as anisotropic exchange coupling constants differ quite appreciably from those obtained recently in a more phenomenological way by the authors of Ref. 10. In particular the tensor elements representing anisotropic exchange are found to be around 1 order of magnitude smaller than those given in the previous work. The anisotropy of the DM interaction is demonstrated in Fig. 7 for the component D_{ij}^x. As one notes D_{ij}^x depends quite strongly in the direction $\hat{R}_{ij}$. In particular one finds D_{ij}^x to be zero, e.g., for the [111] direction due to symmetry. Also because of the symmetry of the system one finds for each direction a symmetry-related one for which the sign of D_{ij}^x is reversed.

The presence of a noncollinear ferromagnetic structure in $Ga_{1-x}Mn_xAs$ is assumed to be partially responsible for the missing of remanent magnetization observed experimentally in annealed samples.[22–24] In particular, the remanent magnetization in this DMS system can be noticeably increased in the presence of a rather small magnetic field. Such a behavior could indeed be explained by the presence of noncollinear magnetism in the system.[23] The anisotropy of the exchange coupling in $Ga_{1-x}Mn_xAs$ was studied theoretically by various authors[10,25–27] to find whether it can be responsible for the formation of a noncollinear ferromagnetic structure as

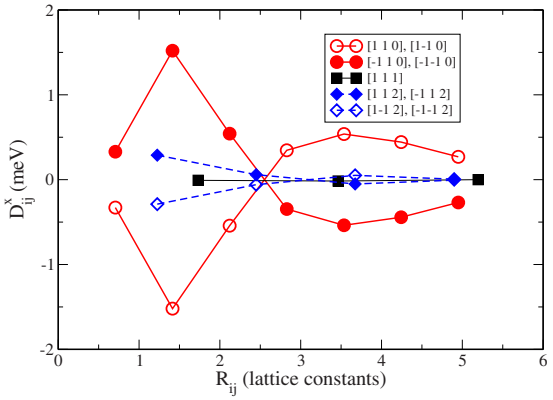

FIG. 7. (Color online) x component of Dzyaloshinski-Moriya interaction $\vec{D}_{ij}$ between Mn atoms at sites i and j in $Ga_{1-x}Mn_xAs$, where $x=0.04$, scaled by the factor $(R_{ij}/a)^2$, as a function of the interatomic distance R_{ij} along different directions.

a ground state in this DMS system. However, these investigations were based on phenomenological or semiphenomenological approach and the results obtained are rather controversial. In contrast to this, the present approach allows us to evaluate the elements of the exchange coupling tensor (in particular, its antisymmetric part representing the DM coupling) on the basis of *ab initio* electronic structure calculations. As was demonstrated above, this leads indeed to a rather large value for the DM coupling in $Ga_{1-x}Mn_xAs$, which is only about 1 order of magnitude smaller than for the isotropic exchange. As mentioned, this finding is in line with the results of Timm and MacDonald.[10] Obviously, the values for the DM coupling term cannot be considered as negligibly small, and as a consequence one cannot exclude a noticeable noncollinear ferromagnetic order in the system. To clarify this question corresponding Monte Carlo simulations based on the calculated exchange tensor will be performed.

IV. SUMMARY

A different scheme to calculate the exchange coupling tensor $\underline{\underline{J}}_{ij}$ has been presented that is based on *ab initio* electronic structure calculations using spin-polarized fully relativistic multiple-scattering theory and spin-density functional theory. Application to ferromagnetic CrTe as well as to other systems demonstrates that the approach gives results for the exchange tensor elements very similar to those obtained using the approach of Udvardi *et al.*[8] However, the present approach makes use of a unique reference state ensuring the internal consistency of the tensor elements. Application to the diluted magnetic semiconductor system $Ga_{1-x}Mn_xAs$ led to an isotropic exchange in full accordance with previous nonrelativistic calculations that were also based on *ab initio* electronic structure calculations. The results obtained for the anisotropic exchange coupling are in accordance with the data of Timm and MacDonald[10] concerning the variation with distance. However, numerically the coupling constants obtained by the present *ab initio* approach and the more phenomenological scheme of these authors differ in an appreciable way.

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