Ab initio calculation of indirect multipolar interactions in DyZn

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We present the results of a calculation of the indirect bilinear and quadrupolar couplings between magnetic ions in the rare-earth intermetallic compound DyZn. We have taken into account the complete rare-earth–conduction-electron (k-f) interaction and we use conduction-electron wave functions and energy bands obtained by a self-consistent augmented-plane-wave calculation. Our results are able to describe reasonably well the extant data on these couplings.

The origin of the coupling between magnetic ions is of fundamental importance in magnetic materials. In metallic systems, it is well known that conduction electrons play an essential role in this coupling by propagating the local interaction between them and the localized magnetic electrons.[1] This indirect exchange mechanism has been widely evoked in rare-earth metals and intermetallic compounds, i.e., the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[2,3] Although this theory has had great success in describing the magnetic properties of many systems, it is incomplete in conventional use by an essential aspect, namely, orbital effects are neglected. The main evidence for such effects is the existence of large quadrupolar interactions in some rare-earth compounds which are able to produce quadrupolar phase transitions, e.g., in TmZn and TmCd.[4–6]

To take into account these orbital effects in an *ab initio* calculation of indirect interactions requires (i) that one does not restrict oneself to gadolinium, an S ion with a spherical symmetry, and (ii) that one considers conduction-electron states which are more realistic than plane waves, for instance, states coming from a band-structure calculation. Up to now, these two conditions have never been taken into consideration *together:* either a free-electron model was assumed for the conduction band and one took into account orbital effects,[7] or a band model was taken but orbital effects were neglected.[8,9]

Here we present the results of the evaluation of the indirect multipolar (bilinear and quadrupolar) interactions in the cubic (CsCl-type structure) ferromagnetic compound DyZn, starting from the energy-band structure and wave functions obtained by a self-consistent augmented-plane-wave (APW) calculation.[10] We emphasize that we have considered the complete k-f Coulomb interaction between the conduction electrons and the $4f$ shell; therefore we find orbital contributions to the conventional isotropic Heisenberg exchange interaction and the quadrupolar pair interactions that are used to interpret the magnetic properties of the cubic rare-earth compounds in the mean-field approximation.[11]

The formalism used for calculating indirect multipolar interactions was previously described.[12] The k-f matrix elements of the direct and exchange Coulomb interactions are evaluated as a function of the coefficients of fractional parentage of the $4f^n$ electrons by using irreducible tensor algebra, and APW wave functions are used for the conduction electrons. By applying second-order perturbation theory we find the effects of the k-f interaction on the electron gas lead to the following effective multipolar Hamiltonian:

$$\mathcal{H} = -\frac{1}{2}\sum_{\nu\nu'}\sum_{KQK'Q'} J_{KQK'Q'}(\nu\nu')O_Q^K(\nu)O_{Q'}^{K'}(\nu') \ , \qquad (1)$$

where $J_{KQK'Q'}(\nu\nu')$ couples the multipolar operators O_Q^K of the νth and ν'th ions. The Fourier transform of the interionic multipolar coefficients may be expressed as

$$J_{KQK'Q'}(\vec{q}) = \sum_{\vec{k}}\sum_{nn'} |I^{n-n'}_{KQK'Q'}(\vec{k},\vec{k}+\vec{q})|^2 \times \frac{f_{\vec{k},n}(1-f_{\vec{k}+\vec{q},n'})}{E_{n'}(\vec{k}+\vec{q})-E_n(\vec{k})} \ , \qquad (2)$$

where $f_{\vec{k},n}$ is the Fermi occupation factor of the conduction state with wave vector $\vec{k}$, band index n, and energy $E_n(\vec{k})$.

Calculations were performed by taking into account the first seven energy bands of DyZn and for eight $\vec{q}$ points in the cubic Brillouin zone (BZ), namely, $\Gamma=(000)$, $X=(400)$, $M=(440)$, $\Lambda_1(111)$, $\Lambda_2=(333)$, $Q_1=(331)$, and $Q_2=(311)$ in units of $\pi/4a$. The last four points were used to evaluate the self-energy terms corresponding to the average values of the $J(\vec{q})$'s over the whole BZ;[13] this self-energy must be subtracted in order to obtain the Fourier transforms of the pair interactions.[14] The summation over $\vec{k}$ in Eq. (2) was made by using the tetrahedron method[15] for $\vec{q}=\Gamma$ and R, with a total of 13 824 $\vec{k}$ points in the whole BZ. For the other $\vec{q}$ points, a discrete summation was made because the preceding method could not be directly applied. This is justified by the fact that an elaborate method is needed only when the denominator is small in Eq. (2).[16] This occurs mainly for $\vec{q}=\Gamma$ and $n=n'=2$ and 3, i.e., the bands crossing the Fermi energy. Finally the three Fourier transforms given in this paper are $\Theta^*(\vec{q})$, $K_1(\vec{q})$, and $K_2(\vec{q})$, which are proportional, respectively, to $J_{1010}(\vec{q})$, $J_{2020}(\vec{q})$, and $J_{212\bar{1}}(\vec{q})$. This allows us to directly compare our calculations with experimental values given in the literature, namely, the isotropic bilinear exchange parameter $\Theta^*=\Theta^*(\Gamma)$ and the tetragonal and trig-

onal quadrupolar parameters $K_1=K_1(\Gamma)$ and $K_2=K_2(\Gamma)$, which are involved in the molecular-field Hamiltonian

$$\mathcal{H}_{\rm MF}=-\frac{3\Theta^*}{J(J+1)}\langle\vec{J}\rangle\cdot\vec{J}-K_1(\langle O_2^0\rangle O_2^0+3\langle O_2^2\rangle O_2^2)$$
$$-K_2(\langle P_{xy}\rangle P_{xy}+\text{cyclic}) \ . \qquad (3)$$

The calculated values of $\Theta^*(\vec{q})$ are given in Fig. 1 for DyZn, together with the experimental ones for the neighboring compound HoZn, as determined from inelastic neutron scattering experiments;[17] these data do not exist for DyZn. The overall agreement of the *form* of the curve $\Theta^*(\vec{q})$ is quite satisfactory, except the small trough around Γ (see below). In particular, the calculated value of $\Theta^*=\Theta^*(\Gamma)$ for DyZn is 153 K, close to the experimental one $\Theta^*_{\rm exp}=140$ K.[18] In order to obtain an idea of the curve $\Theta^*(\vec{q})$ we made a least-squares fit of the eight calculated points to the Fourier series,

$$\Theta^*(\vec{q})=\sum_n\Theta_n^*\sum_j e^{i\vec{q}\cdot\vec{R}_{n,j}} \ , \qquad (4)$$

where the summation over j corresponds to all the vectors $R_{n,j}$ equivalent by the cubic symmetry operations. In this series we kept only the first four terms $n\leq 4$. Aside from providing a four-parameter fit to our data, these Θ_n^* represent the interionic isotropic bilinear coupling coefficients for the first-four-nearest neighbors.

As for the relative contribution of the different bands, it turns out that, without self-energy correction, the main contribution for $\vec{q}$ around Γ arises from the third band, which is principally responsible for the Fermi surface. For $\vec{q}$ values far from Γ, all energy bands must be taken into consideration. However, after correction for the self-energy, both intra- and interband contribution become comparable in size, and generally of opposite sign. For example, the intraband contribution to $\Theta^*(\Gamma)$ is 643 K, and the interband one -490 K, for $\Theta^*(M)$ we find -294 and 42 K, respectively. This cancellation explains the trough of $\Theta^*(\vec{q})$ in the vicinity of Γ by a difference of curvature in this region of the inter- and intraband contributions. It could be one possible explanation for the existence of incommensurate magnetic structures in such metallic systems.[19]

The conduction electrons with d character make the dominant contribution to $\Theta^*(\vec{q})$, in particular those of e_g-type symmetry contribute roughly five times more than the t_{2g}-type electrons. The p electrons account for about 2% of $\Theta^*(\vec{q})$ and the s electrons for less than 0.5%. The remaining contributions to the total $\Theta^*(\vec{q})$ arise from mixed e_g-t_{2g} terms. This result is readily explained by the predominance of d electrons in the vicinity of the Fermi level.[10,20]

In Fig. 2 we show the dependence of $\Theta^*(\vec{q})$ on the Fermi energy E_F for $\vec{q}=\Gamma$, X, M, and R, without self-energy correction. This correction is not necessary for studying the evolution of the magnetic structure as a function of E_F, since the propagation vector $\vec{Q}$ of the actual magnetic structure corresponds to the maximum of $\Theta^*(q)$, for each given E_F. We see that the ferromagnetic structure is the most stable for the number of conduction electrons $N_{\rm el}$ between 4.7 and 5.46 and below 4.6; DyZn with $N_{\rm el}=5$ is situated near the peak of $\Theta^*(\Gamma)$. On each side of this region an antiferromagnetic $(\pi 00)$-type structure, $\vec{Q}=X$, would be favored, as is the case for light rare-earth-zinc compounds.[21] A $(\pi\pi 0)$-type structure, $\vec{Q}=M$, would be stable at higher concentration, while the $(\pi\pi\pi)$-type structure, $\vec{Q}=R$, is never favored. These predictions are very different from a free-electron theory[22] but closer to the experimental situation in these CsCl-type compounds.[19,23] It is worth noting that the peak of $\Theta^*(\Gamma)$ for $E_F=0.424$ Ry is connected with the peak in the partial density of states of d-e_g electrons, since it originates mainly from the intraband $(n=3)$ contribution, and the intraband contribution at $\vec{q}=0$ is directly

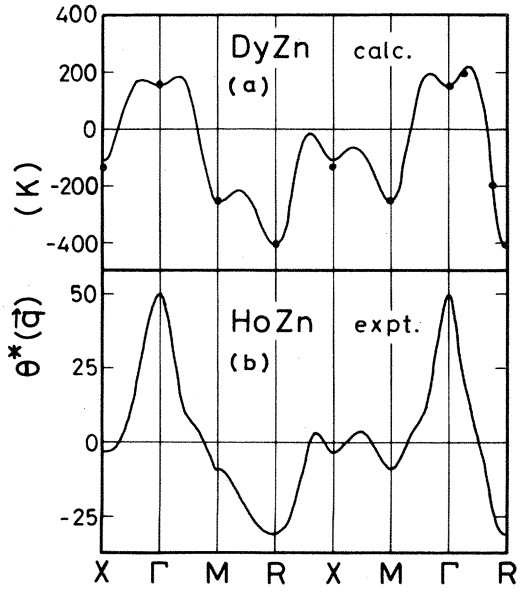

FIG. 1. (a) Fourier transform $\Theta^*(\vec{q})$ of isotropic bilinear interactions in DyZn. Points are calculated, line is a least-squares fit with the coefficient Θ_n^* [see Eq. (4)]: $\Theta_1^*=44.5$ K, $\Theta_2^*=3.4$ K, $\Theta_3^*=1.9$ K, $\Theta_4^*=-27.5$ K. (b) The experimentally determined variation of $\Theta^*(\vec{q})$ for HoZn (see Ref. 17) is given for comparison.

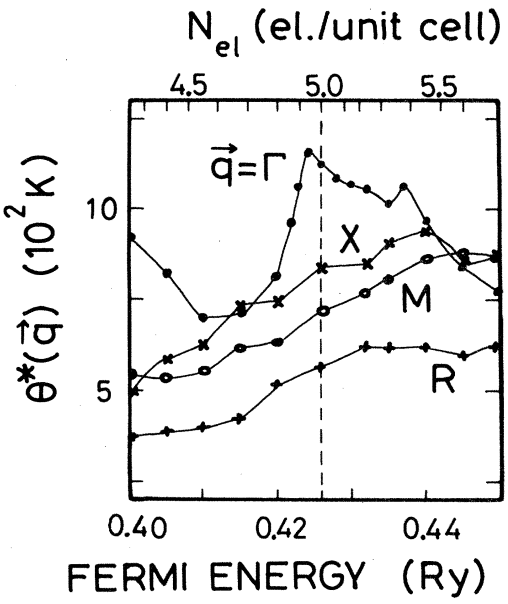

FIG. 2. Dependence of $\Theta^*(\vec{q})$ on the Fermi energy for $\vec{q}=\Gamma$, X, M, and R, including self-energy. The vertical dotted line corresponds to DyZn with $N_{\rm el}=5$ conduction electrons per unit cell.

related to the part of the density of states which corresponds to those conduction electrons around the magnetic ions.[20]

The Fourier transforms of the indirect quadrupolar interactions $K_1(\vec{q})$ and $K_2(\vec{q})$ are given in Fig. 3. The tetragonal quadrupolar interaction $K_1(\vec{q})$ has a $\vec{q}$ dependence similar to $\Theta^*(\vec{q})$, with very negative values for $K_1(M)$ and $K_1(R)$. The only difference is that $K_1(X)$ is larger than $K_1(\Gamma)$, therefore favoring an "antiferroquadrupolar" arrangement of the quadrupoles.

It turns out that all bands contribute to $K_1(\vec{q})$, even at $\vec{q}=\Gamma$. After correction for the self-energy, the intra- and interband contributions are comparable in size but opposite in sign, as for $\Theta^*(\vec{q})$. Similarly the contribution from the d-e_g electron is the dominant one; it is about five times larger than the contribution from the d-t_{2g} electrons. The p electrons contribute roughly 2% of $K_1(\vec{q})$ and s electrons do not contribute at all, since they have no orbital moment. Finally, while the isotropic bilinear interactions involve only an exchange mechanism, there are both direct and exchange contributions to $K_1(\vec{q})$: the total exchange contributions coming from all electrons amount to about -33% of the direct contribution, the p, d-e_g, and d-t_{2g} electron exchange contributions are, respectively, -25%, -45%, and -38% of their direct contributions.

The trigonal quadrupolar interactions, $K_2(\vec{q})$, have a very different behavior from $\Theta^*(\vec{q})$ or $K_1(\vec{q})$; see Fig. 3. $K_2(X)$ and $K_2(M)$ are positive, and $K_2(\Gamma)$ and $K_2(R)$ strongly negative. As for $K_1(\vec{q})$, all bands contribute to $K_2(\vec{q})$ but the *inter*band contributions are the largest. The d-t_{2g} electrons make the dominant contribution to $K_2(q)$ while the d-e_g electrons contribute only indirectly via the mixed e_g-t_{2g} part because by symmetry they have no trigonal quadrupolar matrix elements.

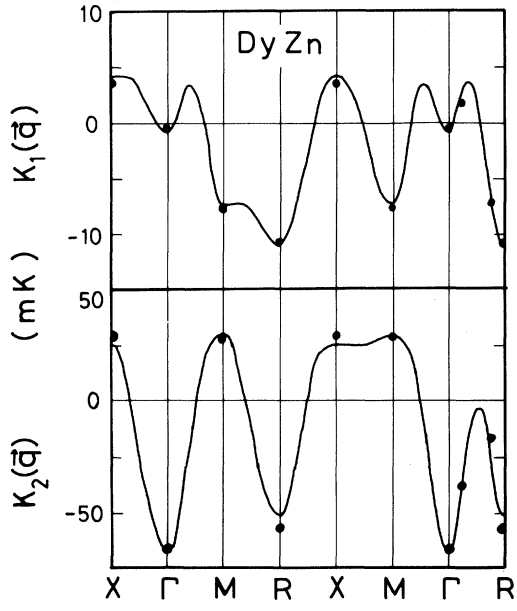

FIG. 3. Fourier transforms $K_1(\vec{q})$ and $K_2(\vec{q})$ of the tetragonal and trigonal quadrupolar interactions in DyZn. Points are calculated, lines are least-squares fits with the coefficient of a Fourier series similar to Eq. (4), with $K_{11}=1.4$ mK, $K_{12}=-0.3$ mK, $K_{13}=-0.4$ mK, $K_{14}=-0.4$ mK, and $K_{21}=-1.3$ mK, $K_{22}=-5.4$ mK, $K_{23}=0$, $K_{24}=0.6$ mK.

In Fig. 4 we show the dependence of $K_1(\vec{q})$ and $K_2(\vec{q})$ on the Fermi energy, where the self-energy has not been subtracted. While $K_1(\Gamma)$ is not the largest for $N_{el}=5$, it is strongly favored as soon as the electron concentration N_{el} decreases. This is mainly due to the interband contribution between second and third bands, which becomes important when E_F is located in between them; indeed the quadrupolar matrix elements $I^{2\text{-}3}_{2020}(\vec{k},\vec{k})$ are very large, both corresponding electron states having primarily e_g character. At higher concentrations ($N_{el}\sim 5.4$) the dispersion of $K_1(\vec{q})$ is very weak and concomitantly the $K_1(\vec{q})$ after correction for the self-energy will be small. On the contrary, the trigonal quadrupolar interactions $K_2(\vec{q})$ have an "antiferroquadrupolar" character for the entire range of electron concentrations.

A final remark concerns the systematic variation of the indirect multipolar interactions across the rare-earth series. While there are orbital contributions to the isotropic bilinear exchange interactions,[24] our calculations show that the spin contribution, i.e., the one that follows the de Gennes factor $(g_J-1)^2J(J+1)$, dominates. Similarly, $K_1(\vec{q})$ and $K_2(\vec{q})$ vary essentially as the square of the Stevens factor α_J. This observation allows us to extrapolate the quadrupolar parameters for DyZn from TmZn. For this compound, various experiments give the values $K_1=20$ mK and $K_2=-90$ mK.[25] By scaling these values to dysprosium by the ratio of the α_J^2's we find K_1 (DyZn) ~ 8 mK and $K_2(\text{DyZn})\sim -36$ mK. Although we calculate a slightly negative $K_1(\vec{q})$ at $\vec{q}=0$, it comes from the same type of cancellation noted above for $\Theta^*(\Gamma)$. Therefore, if we look around the point Γ we see from Fig. 3 that the calculated values for K_1 ($\vec{q}\sim 0$) are comparable to albeit smaller than the extrapolate value. For $K_2(\Gamma)$ we find -66 mK which is in good agreement with the value quoted above.

In summary this *ab initio* calculation of the indirect bilinear and quadrupolar pair interactions in DyZn yields a good overall agreement with the experimental data available on DyZn or isomorphous compounds. The dominant role played by the matrix elements in Eq. (2) is obvious here since they explain the differences between $\Theta^*(\vec{q})$, $K_1(\vec{q})$, and $K_2(\vec{q})$. Our results underscore the predominant effect of the d electrons in the conduction band. In particular,

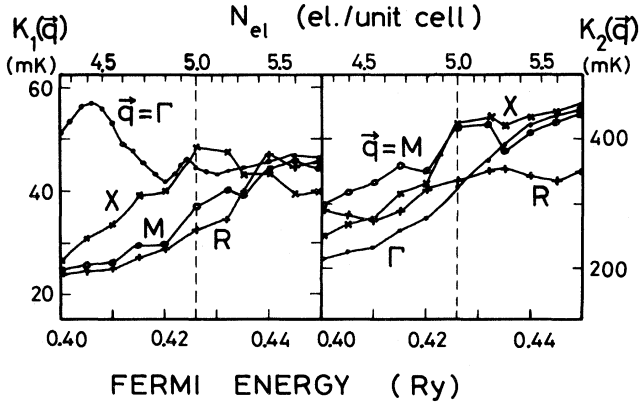

FIG. 4. Dependence of $K_1(\vec{q})$ and $K_2(\vec{q})$ on the Fermi energy for $\vec{q}=\Gamma$, X, M, and R, including self-energy. The vertical dotted lines correspond to DyZn with $N_{el}=5$ conduction electrons per unit cell.

their orbital character is the origin of the strong tetragonal quadrupolar interactions observed in these rare-earth CsCl-type intermetallic compounds. The dependence of the various interactions on the electron concentration has been calculated. For the bilinear coupling, it is in better agreement with the magnetic structures observed in these compounds than previous RKKY calculations based upon a free-electron model. Finally, the quadrupolar parameters are predicted to follow an α_J^2 law, favoring both extremities of the rare-earth series, i.e., Ce, Pr, and Tm ions, which is what has been observed experimentally.

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