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Ab initio calculation of local magnetic moments and the crystal field in $\mathcal{R}_2Fe_{14}B$ ($\mathcal{R}$ = Gd, Tb, Dy, Ho, and Er)

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The local magnetic moments and the valence contribution to the crystal-field parameter A_2^0 at the rare-earth sites are calculated for $\mathcal{R}_2Fe_{14}B$ with $\mathcal{R}$ = Gd, Tb, Dy, Ho, and Er within the framework of the linear-muffin-tin-orbital theory and the local-spin-density approximation. Thereby, the $4f$ moments of $\mathcal{R}$ are calculated by the Russel-Saunders scheme, but the radial $4f$ spin density was part of the self-consistent density-functional calculation. The local moments as well as A_2^0 averaged over the two crystallographically inequivalent $\mathcal{R}$ sites remain remarkably constant across the series.

The ternary intermetallic compounds $\mathcal{R}_2Fe_{14}B$ ($\mathcal{R}$ is a rare earth) are of high technological importance because of their excellent hard magnetic properties (for a review, see Refs. 1 and 2). *Ab initio* calculations of the electronic and magnetic properties represent a big challenge because of the following two reasons: (1) The tetragonal unit cell contains many atoms (68). Therefore, most of the early band-structure calculations[3-7] are empirical or not self-consistent. (2) It is not obvious how to handle the $4f$ electrons, because the strong intraatomic couplings in the $4f$ shell are not adequately described by the usual band-structure calculations based on the local-spin-density approximation (LSDA). Coehoorn[8] therefore has performed self-consistent band-structure calculations only for $\mathcal{R}$ = Gd, where the $4f$ spin-up shell is completely full and the $4f$ spin-down shell is completely empty.

In this paper we report on calculations of the electronic and magnetic properties of $\mathcal{R}_2Fe_{14}B$ with $\mathcal{R}$ = Gd, Tb, Dy, Ho, and Er, based on the linear-muffin-tin-orbital (LMTO) theory[9] using the atomic-sphere approximation (ASA) and the LSDA, adopting the method of Brooks, Nordström, and Johansson[10] for the handling of the $4f$ shell. In this procedure the $4f$ states are treated as open core states, i.e., they are not allowed to hybridize with the conduction-electron states and the number of $4f$ electrons is a fixed integer. Furthermore, the standard Russel-Saunders scheme is applied for a calculation of the projection of the $4f$ spin along the direction of the total $4f$ angular momentum. The $4f$-spin and -electron densities enter the effective potential for the LSDA and are calculated self-consistently, subject to the above constraints (in contrast, in the LSDA calculation of Jaswal[11] for $Nd_2Fe_{14}B$, the $4f$ core states are the frozen self-consistent atomic states). Via this effective potential a coupling between $4f$ and conduction electron states is induced, and hence the influence of different $\mathcal{R}$ atoms on the electronic properties can be studied. This method has already been applied successfully to binary rare-earth intermetallic compounds.[10,12] It will become obvious from our results for the magnetic moments (Table I) that the assumption of a Russel-Saunders coupling for the rare-earth ions considered in this paper is indeed justified.

We calculated the local magnetic moments as well as the crystal-field parameter A_2^0 for the two crystallographically inequivalent $\mathcal{R}$ sites. Because for the series $\mathcal{R}_2Fe_{14}B$ the magnetic anisotropy energy is dominated by the rare-earth contribution (except for $\mathcal{R}$ = Gd), the quantity A_2^0 may be related to the anisotropy under certain circumstances. For transition metals the crystal-field splitting is very large and therefore the orbital moment is strongly reduced. Therefore, the calculation of the anisotropy energy in these systems requires an extremely accurate explicit treatment of the spin-orbit coupling.[13] The situation is somehow easier for rare-earth intermetallics.[1,8,14] In most of these systems the intraatomic Hund's-rule coupling for the $4f$ electrons is much stronger than the exchange coupling between $4f$ states and conduction electron states, which in turn is much stronger than the crystal-field coupling. The strong Hund's-rule coupling ensures that the total angular momentum J of the $4f$ ions is an appropriate quantum number. The second part of the inequality ensures that the magnetic quantum number m_J remains an appropriate quantum number and that the ground state is essentially described by $(J, m_J = J)$. Because this state represents an anisotropic $4f$ charge density, it is finally influenced by the crystal-field interaction, ensuring an orientation of the magnetization along the easy-axis direction. When rotating the magnetization by applying an external magnetic field, the $4f$ charge density is corotated rigidly due to the strong spin-orbit coupling. The related increase of the crystal-field energy corresponds to an increase of the magnetic anisotropy energy (we neglect the conduction electron anisotropy, see above, as well as the feedback of the rotation of the magnetization on the crystal field). It has been pointed out by Givord (cited by Coey[15]) that for all $\mathcal{R}_2Fe_{14}B$ with non-S-state $\mathcal{R}$ ions the room-temperature magnetic anisotropy energy is strongly dominated by the crystal-field parameter A_2^0, which means that the anisotropy constant K_1 is much larger than the higher constants. In this paper, we calculate A_2^0 at zero temperature subject to the restriction of moment alignment along the crystallographic c axis. Because the value of A_2^0 is certainly only weakly temperature dependent, it still makes sense to associate the zero temperature A_2^0 to K_1 at room temperature. Our restriction of spin alignment along the c axis is justified for $\mathcal{R}$ = Gd, Tb, and Dy for all temperatures,[1] whereas for Ho the ground-state spin structure is complex and for Er the zero-temperature easy plane is perpendicular to the c axis. However, the restriction simulates the situation of Ho (Er) at room temperature (slightly above room temperature), where indeed spin alignment along the c axis is observed.[1]

It is convenient to subdivide A_2^0 in a contribution originating from the valence-electron charge density $\rho(\mathbf{R})$ within the atomic sphere (radius r_{AS}) of the considered $\mathcal{R}$ atom $[A_2^0(\mathrm{val})]$ and a contribution originating from the charge density outside $[A_2^0(\mathrm{lat})]$. Zhong and Ching[7] as well as Coehoorn[8] have pointed out that in $\mathcal{R}_2\mathrm{Fe}_{14}\mathrm{B}$ the lattice contribution is probably of secondary importance and that the point-charge model used in many former calculations (for a review see Ref. 1) is unrealistic. According to Ref. 8 $A_2^0(\mathrm{val})$ is given by

$$A_2^0(\mathrm{val})=\frac{\frac{1}{4}\int_{R<r_{\mathrm{AS}}}(3\cos^2\theta-1)\rho(\mathbf{R})d^3R\int_{r<r_{\mathrm{AS}}}(r_<^2/r_>^3)r^2\rho_{4f}(r)dr}{\int_{r<r_{\mathrm{AS}}}r^2\rho_{4f}(r)dr}\,. \tag{1}$$

Here $r_<$ ($r_>$) denotes the smaller (larger) of r and R. In principle, we can use our self-consistent $4f$ charge density both for the numerator and the denominator of (1). However, experimentally[1,16] the product of A_2^0 and the denominator is determined and then A_2^0 is obtained from a division by $\langle r^2\rangle_{4f}$, where for the latter quantity the theoretical results[17] for the free $4f$ ion is inserted. Because we want to compare our results with the experimental values, we also use these theoretical results for the denominator.

To calculate the aspherical valence charge density $\rho(\mathbf{R})$ we first determine by the LMTO-ASA method the self-consistent effective potential, which is spherically symmetric in each atomic sphere. Then the Bloch states for this potential are evaluated by one further LMTO step, yielding the aspherical valence charge density. The feedback of the asphericity of the charge density on the effective potential is neglected. It should be noted that our LMTO approach for the calculation of $\rho(\mathbf{R})$ corresponds to method (b) of Ref. 18, whereas in the original augmented-spherical-wave (ASW) approach[19] a somewhat different procedure is used [method (a)], which is superior for the calculation of the electric-field gradient in hcp metals.

Our LMTO calculations include the combined correction term as discussed in Ref. 20. It turns out that the results for A_2^0 determined without the combined correction term differ by up to a factor of 2. Therefore, technical details of the implementation of the combined correction term are relevant. This becomes important when comparing our results with those of Coehoorn,[8] because in his ASW approach a procedure is used which corresponds to the combined correction term but which is not totally equivalent. We used the scalar relativistic approach of Koelling and Harmon.[21] To test for the influence of different scalar relativistic approaches, we calculated the electric-field gradient for some hcp metals also with the approach of Gollisch and Fritsche[22] and found differences of typically 10%–20%. All calculations have been performed at the experimental lattice constants,[1] and they were converged for 12 k points in the irreducible Brillouin zone.

Our results for the local magnetic moments are presented in Table I. The local moments on the Fe and B sites remain remarkably constant across the series, and the calculated total moments agree excellently with the experimental values reported in Ref. 1. In these calculations we used a fixed atomic-sphere radius of $r_{\mathrm{AS}}=2.688a_0$ for Fe and $r_{\mathrm{AS}}=1.989a_0$ for B, and for $\mathcal{R}$ the radius is chosen in such a way that the sum of all atomic-sphere volumes is equal to the volume of the unit cell, thus taking into account the lanthanide contraction. It should be noted that the moments are only weakly affected by different choices

TABLE I. Local magnetic moments (in μ_B) and total magnetic moment of $\mathcal{R}_2\mathrm{Fe}_{14}\mathrm{B}$. We have used the site notation by Herbst *et al.* (Ref. 23).

$\mathcal{R}$	Gd	Tb	Dy	Ho	Er
$\mathcal{R}$ 4(g)	−7.67	−9.63	−10.58	−10.54	−9.50
$\mathcal{R}$ 4(f)	−7.64	−9.60	−10.55	−10.52	−9.48
Fe 4(e)	2.04	2.03	2.02	2.02	2.02
Fe 4(c)	2.48	2.47	2.44	2.44	2.42
Fe 8(j_1)	2.33	2.32	2.30	2.29	2.28
Fe 8(j_2)	2.60	2.60	2.59	2.59	2.58
Fe 16(k_1)	2.19	2.19	2.17	2.17	2.16
Fe 16(k_2)	2.39	2.39	2.38	2.37	2.36
B 4(f)	−0.18	−0.18	−0.18	−0.18	−0.18
M_s^{calc} (μ_B/f.u.)	17.2	13.2	11.1	11.1	13.1
M_s^{expt} (μ_B/f.u.)	17.9	13.2	11.3	11.2	12.7

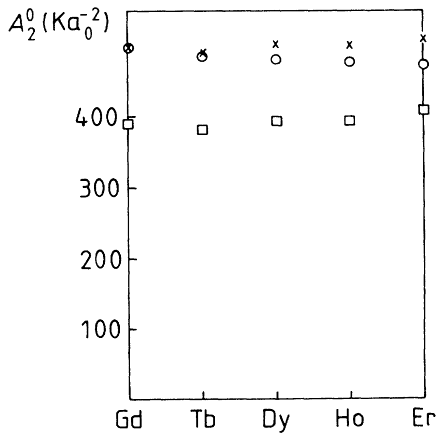

FIG. 1. The valence contribution $A_2^0(\mathrm{val})$ averaged over the two crystallographically inequivalent $\mathcal{R}$ sites, for different choices of atomic-sphere radii. (×) $r_{\mathrm{AS}}(\mathcal{R})$:$r_{\mathrm{AS}}(\mathrm{Fe})$:$r_{\mathrm{AS}}(\mathrm{B})$ $=1.35$:1:0.74; (○) including the lanthanide contraction as in Table I, see text; (□) $r_{\mathrm{AS}}(\mathcal{R})$:$r_{\mathrm{AS}}(\mathrm{Fe})$:$r_{\mathrm{AS}}(\mathrm{B})=1.25$:1:0.73.

of the atomic-sphere radii. However, it turns out that A_2^0 depends rather sensitively on the atomic-sphere radii (Fig. 1), in contrast to the finding of Coehoorn.[8] One possible reason for this discrepancy may be the different implementation of the combined correction term (see above) which corrects for the overlap of the atomic spheres. Furthermore, we obtain different $A_2^0(\text{val})$ values for the two crystallographically inequivalent $\mathcal{R}$ sites (between about 25% and 50%), again in contrast to Coehoorn,[8] probably because of the same reason (the overlap of the atomic spheres is drastically different for the different $\mathcal{R}$ sites). In Fig. 1 we present $A_2^0(\text{val})$ averaged over the two lattice sites. When we want to compare our results for $\mathcal{R}=\text{Gd}$ with the one of Coehoorn[8] we must use the same atomic-sphere radii (symbols × or ○ in Fig. 1). Furthermore, we must insert (as Coehoorn did) for $\langle r^2\rangle_{4f}$ the self-consistent value obtained in our calculation instead of the free-ion value used in Fig. 1. This changes A_2^0 by about 20%. Finally, we must subtract from our value the contribution of the so-called cross term, which has been neglected by Coehoorn but taken into account in our calculation, again changing A_2^0 by about 20%. This yields a value of $A_2^0=338\ \text{K}a_0^{-2}$, which compares to $A_2^0=376\ \text{K}a_0^{-2}$ of Coehoorn.

In agreement with experiment,[16] our values for A_2^0 remain remarkably constant through the series. This as well as the insensitivity of the iron moments confirm the experimental finding of Sellmyer *et al.*[24] that all compounds of the form $\mathcal{R}_2\text{Fe}_{14}\text{B}$ have very similar electronic structures except for the $4f$ levels. The experimental values of about 300 $\text{K}a_0^{-2}$ are smaller than our values (Fig. 1). The discrepancy is not astonishing because we have neglected the lattice contribution. We have estimated this contribution by a point charge model using the calculated charges in the atomic spheres. Typically, we obtain $A_2^0(\text{lat})$ values of the order of $-100\ \text{K}a_0^{-2}$, improving the agreement with the experimental values. It will be of interest to calculate the lattice contribution more accurately from the aspherical charge density outside the considered atomic sphere.

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