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2002 J. Phys.: Condens. Matter 14 10273

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## Theory of crystal field states for heavy rare-earth impurities in MgB<sub>2</sub>

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Received 4 July 2002

Published 18 October 2002

Online at [stacks.iop.org/JPhysCM/14/10273](http://stacks.iop.org/JPhysCM/14/10273)

### Abstract

For isolated rare-earth impurities substituting for Mg atoms in the superconductor MgB<sub>2</sub> the crystal field parameters are calculated by the *ab initio* density functional electron theory with constraints for the 4f charge and spin density. The crystal field parameter  $A_0^6$  is extremely small due to the structure and bonding properties of MgB<sub>2</sub>, and therefore the crystal field levels are nearly exclusively determined by one magnetic quantum number  $M$ . Implications for the pair-breaking mechanism of the superconductivity in MgB<sub>2</sub> are discussed.

The discovery of superconductivity close to 40 K in the binary non-oxocuprate inorganic material MgB<sub>2</sub> by Nagamatsu *et al* [1] stimulated extensive investigations aimed at achieving an understanding of the superconducting state and increasing  $T_c$  beyond 40 K, e.g., by suitable doping with other transition metal atoms.

MgB<sub>2</sub> crystallizes with a hexagonal AlB<sub>2</sub> structure type which contains planar B honeycomb layers and close-packed Mg layers with the Mg atoms centred in the B hexagons (see below). This structure type is also adopted by some rare-earth (RE) diboride phases MB<sub>2</sub>, with M standing for the magnetic heavy RE metals Tb, Dy, Ho and Er but also non-magnetic Sc and Y [2, 3]. The structural and magnetic properties of these MB<sub>2</sub> phases were investigated in more detail by Will and Schäfer [4] some time ago. The RE ions were all found to be in the oxidation state 3+ with effective magnetic moments appropriate to the respective 4f<sup>*n*</sup> configurations. It has been concluded that the magnetic ordering scheme is more complex than the simple collinear ferromagnetic one and ordering temperatures up to 151 K (TbB<sub>2</sub>) have been found [4, 5]. Low-temperature saturation magnetic moments point to a considerable influence of crystal electric fields leading to a splitting of the respective  $J$ -manifolds and a reduction of the ground state moments from the free-ion  $g_J J$ -values. While the effects on the superconducting properties of MgB<sub>2</sub> of doping with most of the possible d-metal species, e.g. Mn, V, Cr, have been investigated in detail, it appears that doping with RE atoms has, so far, received only little attention.

There has been extensive research in the last few decades concerning the question of how the properties of free ions exhibiting non-closed inner electronic shells with Hund's rule coupling are modified when these ions are embedded in a crystal. For the case of the transition metal ions the crystal field interactions of the 3d electrons are often intermediate or strong, so they cannot be treated as a perturbation and thus lead to strong modifications of the magnetic moments (see, e.g., [6]). In contrast, the crystal field interactions of RE ions are often weak and can be treated in a perturbative manner (at least at temperatures much larger than the Kondo temperatures, which are of measurable size only for Ce and Yb). As a result, the RE ions in a crystal are usually in a trivalent configuration (with the exception of Ce) which resembles very much the Hund's rule ground state configuration of the respective free ion with total angular momentum  $J$ , i.e., mixing with excited multiplet states can be neglected. The main effect of the crystal surroundings is to lift the degeneracy with respect to the magnetic quantum number  $M$ . In ferromagnetic materials the degeneracy is dominantly lifted by the exchange interactions, selecting the maximum  $M$  such that the exchange energy is maximum. The crystal field interactions are then responsible for the magnetic anisotropy [7]. In contrast, in non-magnetic materials the crystal field interactions themselves are responsible for a lifting of the degeneracy, leading to a mixing of various  $|M\rangle$  states [8] for the wavefunctions  $|\Psi_i\rangle$ :

$$|\Psi_i\rangle = \sum_M c_i^M |M\rangle. \quad (1)$$

It has been shown [9, 10] that crystal field splitting effects of RE impurities can modify substantially the pair breaking in superconductors originally described by Abrikosov and Gorkov [11]. Two competing mechanisms for the change of the critical temperature  $T_c$  have been proposed. The first and usually dominant one is the exchange interaction which reduces  $T_c$  and which may be operative even for RE dopants with non-magnetic ground states via off-diagonal matrix elements. The second one is the inelastic charge scattering of conduction electrons at the aspherical 4f charge density, leading to an enhancement of  $T_c$ . Both mechanisms have an effect on  $T_c$  even for crystal field levels at energies far above  $k_B T_c$ . Which mechanism dominates depends on the symmetry character of the levels involved; in favourable cases it may be possible to separate the two types by considering various RE impurities. The dependence of  $T_c$  on the impurity concentration  $x$  can be calculated within the framework of the theory of [9, 10] provided that the various crystal field states are known. Comparing the results with experimental data could at least in principle serve as a test for the validity of the various assumptions underlying the theory—for instance, the assumption of only s-state superconducting pairing via a constant attractive potential  $V$  leading to an isotropic order parameter  $\Delta$ . Finally, it has been shown [9] that the crystal field levels of the impurities should give rise to a structure in the superconducting tunnelling characteristics by which the crystal field splittings can possibly be observed more directly than by most other methods.

In the present paper we calculate by means of *ab initio* electron theory the crystal field levels and the crystal field states for heavy RE ions in the superconductor  $\text{MgB}_2$ . Such investigations are interesting from various viewpoints. First, in  $\text{MgB}_2$  the B atoms reside in graphite-like honeycomb layers and the Mg atoms are above and below the centres of the  $\text{B}_6$  rings (see above). The material is held together by strongly covalent bonds within the B layers and by delocalized metallic-like bonding between the B layers (with a more homogeneous charge distribution) where the Mg atoms are located. The question is how this special structure is reflected in the values of the crystal field parameters, as compared to the respective values for insulator-like RE ethylsulphates and RE chlorides [8] or metallic RE ferromagnets [12–14] such as  $\text{RECo}_5$ . Second, superconductivity in  $\text{MgB}_2$  originates from the coupling of the holes in the B  $p_{x,y}\sigma$ -bands to the intralayer B bond-stretching phonon modes [15]. The question then arises of whether doping with RE impurities substituting for the Mg atoms which are

located outside the B layers really has a significant influence on the superconducting pairing mechanism. For the case of Mn atoms substituting for Mg, it has been demonstrated [16] that there is indeed a strong effect on  $T_c$ . Finally, by comparing the calculated  $T_c(x)$  curves determined on the basis of the *ab initio* calculated crystal field parameters with respective experimental curves for various types of RE ion, it may be possible to learn something about the properties of the pairing mechanism in MgB<sub>2</sub> (see above), e.g., on the possibility of an anisotropic gap or multiple gaps [18].

Because of the hexagonal symmetry at the RE site in MgB<sub>2</sub> (point symmetry C<sub>3h</sub>), the crystal field Hamiltonian  $\hat{H}_{CF}$  may be written as [7, 8]

$$\hat{H}_{CF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_6^0 \hat{O}_6^0 + B_6^6 \hat{O}_6^6. \quad (2)$$

Here the  $\hat{O}_n^m$  are the equivalent operators which are given by combinations of the components of the operator  $\hat{J}$  of the total angular momentum of the RE ion. The  $B_n^m$  are given by

$$B_n^m = A_n^m \langle r^n \rangle_{4f} \theta_{J,n}, \quad (3)$$

where  $A_n^m$  are the crystal field parameters;  $\langle r^n \rangle_{4f}$  are the expectation values of  $r^n$  for the RE<sup>3+</sup> ions; and  $\theta_{J,n}$  are the Stevens factors which are tabulated for each RE<sup>3+</sup> ion [7, 8]. The quantum mechanical state of the RE<sup>3+</sup> ion in the crystal field described by  $\hat{H}_{CF}$  is determined by degenerate perturbation theory based on the ansatz (1), and hence the crystal field levels are obtained by diagonalizing the matrix  $\langle M | \hat{H}_{CF} | M' \rangle$ . Thereby the operators  $\hat{O}_n^0$  have only diagonal matrix elements, whereas  $\hat{O}_6^6$  has only non-diagonal matrix elements [8]. For Kramers ions which have half-integer values of  $J$ , the wavefunctions  $|\Psi\rangle$  in the crystal field are Kramers doublets consisting of linear combinations of the form

$$|\Psi\rangle = c^{M+6} |M+6\rangle + c^M |M\rangle + c^{M-6} |M-6\rangle. \quad (4)$$

For non-Kramers ions with integral values of  $J$ , there is a series of doublets of the form (4) and singlets of the form  $|3\rangle \pm |-3\rangle$ ,  $|6\rangle - |-6\rangle$  and  $\alpha(|6\rangle + |-6\rangle) + \beta|0\rangle$ . The various crystal field levels can be classified according to the irreducible representations of the point symmetry group of the RE site [9].

In the present paper we determine the crystal field states of the RE<sup>3+</sup> ions in MgB<sub>2</sub> by a procedure which is iterative in principle. In a first step we neglect the mixing of the various  $M$ -states and assume that the RE<sup>3+</sup> ion is in the state  $|J, M = J\rangle$  as if it was in a ferromagnetic host. We then calculate the crystal field parameters  $A_n^m$  experienced by the RE<sup>3+</sup> ions in that state by means of density functional electron theory in the local spin-density approximation (LSDA [20]); see below. The non-4f states thereby feel the spin density of the RE<sup>3+</sup> ion in the state  $|J, M = J\rangle$  via the exchange–correlation potential of the density functional theory. In a second step the crystal field states  $|\Psi\rangle$  are determined for the set of crystal field parameters  $A_n^m$  obtained by the procedure described above. In general, the resulting crystal field states are different from the state  $|J, M = J\rangle$  used for the calculation of the  $A_n^m$ ; for instance, they have other spin densities. In principle, we should therefore perform a second iterative step, starting from the respective crystal field states obtained in the first step, recalculate the crystal field levels and repeat the procedure until convergence is achieved. In fact, it turns out that the crystal field parameters change only slightly when going from the spin density of the state  $|J, M = J\rangle$  to the spin density of another state. For instance, for Tb in MgB<sub>2</sub> the crystal field parameter  $A_2^0$  changes by less than 10% when going from the magnetic  $|J, M = J\rangle$  Tb<sup>3+</sup> ion to an artificial Tb<sup>3+</sup> ion for which we switch off the magnetic moment, and the changes of the other  $A_n^m$  are negligible. We therefore confine ourselves to the first iteration step in all our further calculations.

The crystal field parameters are determined to a very good approximation by the electrostatic interaction of the aspherical 4f charge density  $\rho_{4f}(\underline{r})$  with the Coulomb potential

$V(\underline{r}) = \sum_{n,m} V_n^m(r) Z_n^m(\theta, \phi)$  (the  $Z_n^m$  are cubic harmonics) produced by all the other charges in the system. In this approximation the crystal field parameters are given by

$$A_n^m = c_n^m \frac{\int dr r^2 \rho_{4f}(r) V_n^m(r)}{\int dr r^2 \rho_{4f}(r) r^n}, \quad (5)$$

where the  $c_n^m$  are numerical factors. In reality there is a small additional contribution to  $A_n^m$  [21] arising from the exchange–correlation potential which we have taken into account. It has been shown by second-order perturbation theory [21–23] that for the calculation of the  $V_n^m(r)$  a spherically averaged 4f charge density  $\rho_{4f}(r)$  has to be used instead of the strongly anisotropic density. In equation (5)  $\rho_{4f}(r)$  is a function which is well localized in the interior of the atomic sphere surrounding the RE<sup>3+</sup> ion, whereas  $V_n^m(r)$  is small in the centre of the atomic sphere and increases gradually when approaching the sphere boundary. The  $A_n^m$  are therefore determined by the small overlap of the two functions  $\rho_{4f}(r)$  and  $V_n^m(r)$  which therefore have to be determined with extreme care. The non-4f states (which contribute to  $V_n^m(r)$ ) are determined in the LSDA by the WIEN 97 code [24] which is based on the full-potential linearized augmented-plane-wave (FLAPW) method [25]. Spurious 4f valence contributions arising from the deficiency of the LSDA in describing the 4f states are removed by choosing negative 4f augmentation energies [12], and the energetically high-lying 5p states of the RE<sup>3+</sup> ion are included in the valence via local orbitals [26]. The 4f charge density  $\rho_{4f}(r)$  is not determined by the LSDA because of the well-known deficiency of the LSDA in handling 4f states. Instead, we adopt the standard model of RE ions in metals [12, 27] which assumes that the anisotropic charge density of the 4f shell is basically the same as that of a free trivalent RE<sup>3+</sup> ion. We therefore insert essentially [12] the 4f charge and spin density of the free RE<sup>3+</sup> ion in the state  $|J, M = J\rangle$  as obtained by a fully relativistic Dirac–Fock calculation with configuration interaction [28].

The calculations are performed for a supercell geometry; i.e., large supercells of MgB<sub>2</sub> containing 95 sites and one RE atom are arranged periodically, and the structural relaxations of the atoms around the impurity are taken into account. Table 1 compares for the case of a Tb impurity the results for  $A_n^m \langle r^n \rangle_{4f}$  as obtained from calculations with and without relaxation and for various numbers of  $k$ -points used for the sampling of the irreducible Brillouin zone. It demonstrates that in order to obtain reliable results for the crystal field parameters, it is indispensable to perform the structural relaxation and to go beyond the  $\Gamma$  point approximation for the sampling of the Brillouin zone. Basically the same behaviour as in the case of Tb was found for Dy impurities. To obtain nearly converged results we should in principle perform the structural relaxation and the final calculation of the  $A_n^m$  with at least nine  $k$ -points in the irreducible Brillouin zone of the 96-atom supercell. Because this is extremely costly, we perform the calculations for the whole series of heavy RE atoms by relaxing the structure just at the  $\Gamma$  point and performing the final calculation of the  $A_n^m$  for the so-obtained structure for nine  $k$ -points in the irreducible Brillouin zone.

Table 2 compiles our results for the heavy RE impurities in MgB<sub>2</sub>. In table 3 we compare for the case of Tb (very similar results hold for all the heavy RE ions) our data with those for the two hexagonal salts [8] RE ethylsulphate and anhydrous RE chloride and for TbCo<sub>5</sub> [12]. Whereas  $A_2^0 \langle r^2 \rangle_{4f}$  and  $A_4^0 \langle r^4 \rangle_{4f}$  have the same sign and are of about the same size for the two salts and for Tb in MgB<sub>2</sub>, the quantities  $A_6^0 \langle r^6 \rangle_{4f}$  and  $A_6^6 \langle r^6 \rangle_{4f}$  have different signs and are one and two orders of magnitude smaller for the case of MgB<sub>2</sub>. Altogether, the most striking result is the extreme smallness of  $A_6^6 \langle r^6 \rangle_{4f}$  for the RE impurities in MgB<sub>2</sub>, i.e., the magnetic energy is nearly rotationally invariant around the hexagonal axis. We ascribe this finding to an almost homogeneous charge distribution between the B layers where the RE impurities are located (see above).

**Table 1.** Results for  $A_n^m \langle r^n \rangle_{4f}$  in kelvins for the Tb impurity in MgB<sub>2</sub>. The headings ‘No relaxation’ and ‘Relaxation’ indicate calculations without and with structural relaxation. The quantity ‘ $nkr$ ’ is the number of  $k$ -points (for the irreducible Brillouin zone) used for the structural relaxation and ‘ $nk$ ’ is the number of  $k$ -points used for the final calculation of the crystal field parameters for a given structure.  $nk = 1$  and  $nkr = 1$  denote calculations at the  $\Gamma$  point.

	No relaxation			Relaxation				
				$nkr = 1$			$nkr = 4$	$nkr = 9$
	$nk = 1$	$nk = 4$	$nk = 9$	$nk = 1$	$nk = 4$	$nk = 9$	$nk = 4$	$nk = 9$
$A_2^0 \langle r^2 \rangle_{4f}$	186.1	85.9	65.3	249.3	146.5	147.4	132.6	118.3
$A_4^0 \langle r^4 \rangle_{4f}$	-33.7	-46.9	-44.5	-42.9	-57.2	-55.0	-56.9	-53.5
$A_6^0 \langle r^6 \rangle_{4f}$	5.4	5.0	5.0	5.1	4.8	4.8	4.3	4.3
$A_6^6 \langle r^6 \rangle_{4f}$	-9.6	-10.3	-10.6	-0.7	-1.3	-1.5	-2.0	-3.5

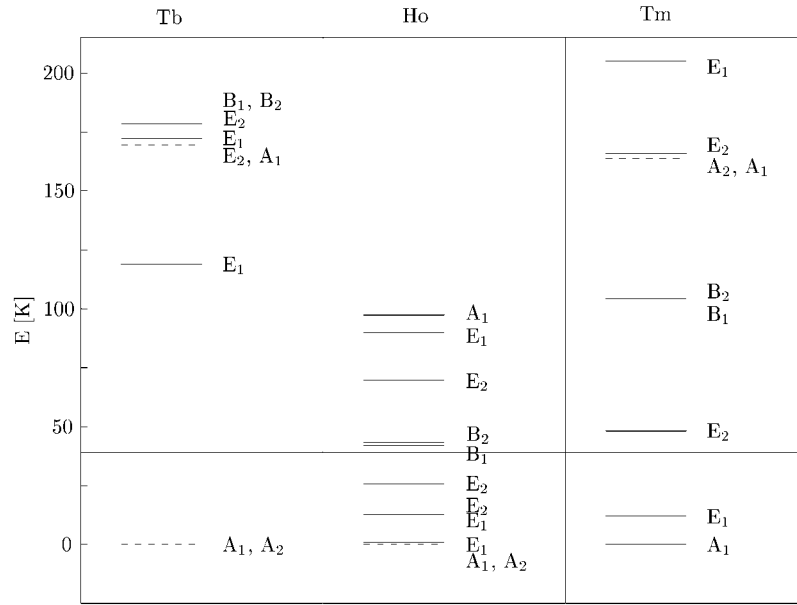
**Table 2.** Results for  $A_n^m \langle r^n \rangle_{4f}$  in kelvins. The calculations are for  $nkr = 1$  and for  $nk = 9$  (see table 1 caption).

	Tb	Dy	Ho	Er	Tm
$A_2^0 \langle r^2 \rangle_{4f}$	147.4	153.2	157.4	161.6	165.8
$A_4^0 \langle r^4 \rangle_{4f}$	-55.0	-54.6	-53.8	-53.5	-52.6
$A_6^0 \langle r^6 \rangle_{4f}$	4.8	4.5	4.1	3.9	3.6
$A_6^6 \langle r^6 \rangle_{4f}$	-1.5	-2.1	-3.0	-3.0	-3.5

**Table 3.** Comparison of  $A_n^m \langle r^n \rangle_{4f}$  in kelvins for Tb in various materials.

	Ethylsulphate [8]	Chloride [8]	MgB <sub>2</sub>	TbCo <sub>5</sub> [12]
$A_2^0 \langle r^2 \rangle_{4f}$	158.3	132.4	147.4	-254
$A_4^0 \langle r^4 \rangle_{4f} / A_2^0 \langle r^2 \rangle_{4f}$	-0.682	-0.435	-0.373	0.064
$A_6^0 \langle r^6 \rangle_{4f} / A_2^0 \langle r^2 \rangle_{4f}$	-0.31	-0.326	0.033	-0.006
$A_6^6 \langle r^6 \rangle_{4f} / A_2^0 \langle r^2 \rangle_{4f}$	4.23	3.15	-0.01	0.188

With the values  $A_n^m \langle r^n \rangle_{4f}$ , the crystal field levels and the crystal field states  $|\Psi\rangle$  can be calculated easily by means of the perturbation theory described above. Because the  $A_6^6 \langle r^6 \rangle_{4f}$  are so small for the systems considered in this paper, the Hamiltonian matrix  $\langle M | \hat{H}_{CF} | M' \rangle$  is nearly diagonal and hence the crystal field levels are mainly determined by one component,  $|M\rangle = |M^{dom}\rangle$ , which is determined by the actual values of  $A_2^0$ ,  $A_4^0$  and  $A_6^0$ . For the crystal field ground states of Tb, Dy, Ho, Er and Tm we find that the dominant  $|M\rangle$  component is  $|M^{dom}\rangle = 6, 13/2, 6, 1/2$  and  $0$ , respectively. In the following we do not consider further the Kramers ions Dy and Er with  $J = 15/2$  for which all crystal field states are doublets and for which exchange scattering of the valence electrons is always allowed. We concentrate on the non-Kramers ions Tb ( $J = 6$ ), Ho ( $J = 8$ ) and Tm ( $J = 6$ ). For them there are also singlet crystal field levels with no elastic exchange scattering. For such systems it is conceivable that the scattering of valence electrons is dominated by two low-lying singlet levels connected by aspherical charge scattering with inelastic exchange scattering forbidden, with the result that the respective RE impurities should cause an increase of  $T_c$ . Figure 1 shows the various crystal field levels classified according to the irreducible representations of the point group of



**Figure 1.** The crystal field levels for Tb, Ho and Tm impurities in MgB<sub>2</sub>. For the meanings of the representation labels see table 3 of [9]. All ground state levels are normalized to zero energy. Broken lines denote two crystal field levels which are nearly degenerate. The horizontal line denotes the critical temperature of MgB<sub>2</sub> ( $T_c = 39$  K).

the crystal (see table 3 of [9]). For all three ions the crystal field ground state in zero field is a non-magnetic singlet of symmetry  $A_1$  with  $|\Psi\rangle = \alpha(|6\rangle + |-6\rangle) + \beta|0\rangle$ . However, it becomes obvious from the selection rules given in table 5 of [9] that in view of the symmetries of the low-lying crystal field states the scattering of the valence electrons will always be dominated by exchange processes. Furthermore, and even more important, the crystal field mixing of the states  $|6\rangle$ ,  $|-6\rangle$  and  $|0\rangle$  induced by the very small term  $A_6^6$  is so small that we have  $\alpha \gg \beta$  for Tb and Ho according to  $M^{dom} = 6$  and  $\alpha \ll \beta$  for Tm according to  $M^{dom} = 0$ . This means that the crystal field interactions induced by the  $A_6^6$ -term are already smaller than the Zeeman interactions for very small magnetic fields. Therefore, for realistic experimental situations the Tb<sup>3+</sup> ion in MgB<sub>2</sub> will exhibit the magnetic moment of the state  $|J, M^{dom} = 6\rangle$  and hence give rise to strong elastic exchange scattering of the valence states. Accordingly, in finite magnetic fields the other RE<sup>3+</sup> ions in MgB<sub>2</sub> also will attain the magnetic moments of the state  $|J, M = M^{dom}\rangle$ .

It should be noted that for the case of Ho there are many crystal field levels with excitation energies smaller than  $k_B T_c$  which should give rise to a rich structure in the superconducting tunnelling characteristics [9], in striking contrast to the case for Tb.

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