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Calculation of crystal-field parameters in the RNi$_5$ (R=rare earth) system

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We report an *ab initio* calculation of the crystal-field parameters b_{lm} of rare-earth ions in intermetallic RNi$_5$ compounds. The parameter with given l and m is calculated by integrating the product of the aspherical (l,m) component of the crystal potential and the radial density of $4f$ electrons of the rare-earth ion. The potential results from the self-consistent calculation of the electronic structure of RNi$_5$ using the full potential linear-augmented plane-wave method, while the density of the $4f$ electrons is taken from a local-density approximation–self-interaction correction atomic calculation. The calculated parameters are then compared with parameters obtained by other authors from the analysis of experimental results.

I. INTRODUCTION

Intermetallic compounds RNi$_5$ (R=rare earth) exhibit a variety of interesting physical phenomena. Many of these phenomena are connected with the splitting of the multiplets of R ions by the crystalline electric field. In PrNi$_5$ this splitting leads to a well isolated singlet ground state of the Pr ion[1] and as a consequence the exchange interaction between the Pr ions is very weak and the system does not order magnetically to very low temperatures. In other RNi$_5$ compounds the interplay between the crystalline electric field, spin-orbit coupling, and the exchange interaction is the source of the R ion's magnetocrystalline anisotropy which usually prevails at low temperatures.[2] Its strong temperature dependence may then lead to spin-reorientational transitions at the elevated temperatures.

RNi$_5$ compounds crystallize in the hexagonal CaCu$_5$ structure (space group $P6/mmm$) and the point symmetry of the R site is D_{6h}. In this symmetry the effective Hamiltonian which describes the splitting of the $4f$ levels of the R ion in the crystal has the form

$$\hat{H} = b_{20}\hat{O}_{20} + b_{40}\hat{O}_{40} + b_{60}\hat{O}_{60} + b_{66}\hat{O}_{66}, \qquad (1)$$

where b_{lm} are the crystal field parameters (CFP) and $\hat{O}_{lm}$ are the Stevens operators. CFP's are usually determined by comparing the experimental results with theoretical predictions based on (1). The values of such obtained CFP's are often unreliable, however—usually the analysis of the experimental results involves additional assumptions, in many cases not enough independent experimental data are available, and in the magnetically ordered systems it is difficult to distinguish the effect of the crystalline field from the effect of an anisotropic exchange interaction.

There exist a number of the CFP sets obtained by the analysis of various experimental results in the RNi$_5$ compounds. In Table I we summarize those CFP sets which either are the most reliable (in the sense that the corresponding analysis included more experimental data comparing to the CFP sets omitted from Table I) or are obtained from independent experiments. We note that the values of CFP's for PrNi$_5$ seem to be very reliable comparing to the situation in other intermetallic rare-earth systems—PrNi$_5$ does not order magnetically and virtually the same set of CFP's was obtained by three different experimental methods. The RNi$_5$ system and in particular the PrNi$_5$ compound are therefore convenient for testing various theoretical approaches to the calculation of CFP's.

Theoretical determination of CFP's of the rare-earth ions in intermetallic compounds is a longstanding problem. Early attempts to determine CFP's were based on rather naive point charge models for the distribution of electronic charge and only recently were more realis-

TABLE I. RNi$_5$ compounds. Values of crystal-field parameters (in K) deduced from various experiments. α_l are the Stevens factors.

R	b_{20}/α_2	b_{40}/α_4	b_{60}/α_6	b_{66}/α_6	Ref.
Pr	-278	-62	14.5	515	1
	-276	-71	13.1	508	3
	-282	-63	14.8	495	4
Nd	-522	-50	9.2	355	5
	-397	-216	10	369	6
Tb	-380	-3	36	357	7
	-380	-20	0.5	327	8
	-363	-15	1	327	9
Ho	-518	-55	1.6	232	10
	-520	-22	7.2	206	11
Er	-242	-56	11.2	64	12
	-276	-22	24.1	145	13
Tm	-376	-7	-33	136	14

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tic charge distributions, resulting from the self-consistent band calculations, used.[15–19]

The aim of the present paper is to calculate CFP's for the whole $R\mathrm{Ni}_5$ series. To solve the problem we have to know the crystal potential and the density distribution of the $4f$ electrons. The crystal potential is determined from a self-consistent band calculation described in Sec. II A, while (as shown in Sec. II B) the $4f$ electron density should be calculated separately. To this end we perform the atomic calculation with a self-interaction correction included. Our calculation gives the trends of CFP's as function of R and, unlike in most other papers, all CFP's compatible with the symmetry (and not only b_{20}) are determined.

II. THEORETICAL METHOD

A. Band calculations

To determine the electronic band structure of $R\mathrm{Ni}_5$ we used a slightly adapted Wien package of programs[20] which is based on the full potential linearized augmented plane-wave (FLAPW) method. The FLAPW method belongs to the most accurate methods of the band calculations—in particular no averaging of either potential or electronic density is made. This makes FLAPW especially suitable for the calculation of quantities connected with the anisotropy of the charge distribution (electric field gradient, CFP).

In the FLAPW method the crystal is divided into spheres surrounding each atom and the remaining interstitial region. Inside the atomic spheres the potential is expanded using the spherical harmonics:

$$V(r) = \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} V_{lm}(r) Y_{lm}(\vartheta,\varphi) \tag{2}$$

while in the interstitial region the plane-wave representation of the potential is used. The electronic density is represented analogously. The potential is written as a sum of Coulomb and exchange-correlation terms:

$$V = V_{\mathrm{Coul}} + V_{\mathrm{xc}}. \tag{3}$$

In our calculation V_{xc} in the form given by Hedin and Lundqvist[21] was used.

As usual in the FLAPW method the electronic states are divided into several groups:[20] valence states ($5d$, $6s$, $6p$ states of R; $3d$, $4s$, $4p$ states of Ni); semicore states ($5s$ and $5p$ states of R); and core states which in our case comprise the remaining electronic states of both R and Ni except the $4f$ states of R, which are treated separately (see below). Core electrons are treated fully relativistically, while for the remaining electrons only scalar relativistic corrections are included.

The $4f$ electrons—because of their strong correlation and charge inhomogeneity—cannot be correctly described by the band calculation. Using the experimental evidence, it is possible, however, to model the $4f$ system well enough for sufficiently accurate description of the rest of electron system. The experiment shows that in the systems considered the $4f$ electrons are well localized; their number on each R ion follows from the R^{3+} valence state and in the ground state the electrons are arranged so that the spin of the R^{3+} ion is maximal. Such premises were successfully used by many other authors when calculating the electron structure of similar rare-earth compounds. In some of the recent papers the $4f$ states are treated as the "open core states," i.e., as states belonging to the core in which the $4f$ electrons are arranged in accord with the above requirements. In our case, however, the energy of $4f$ states is rather high, which causes an instability when treating them as a part of the core. For this reason we prefer to consider the $4f$ states as a separate group of semicore levels. When using this approach, several precautions must be made, however.

(i) The nonspherical part of the $4f$ electron density must be set equal to zero. In this way a contribution to the CFP's arising from the interaction of $4f$ electrons with the potential they create themselves (self-interaction) is avoided.

(ii) Dispersion of the $4f$ states is prevented by solving the eigenvalue problem for the $4f$ semicore states in the Γ point only.

B. Calculation of crystal-field parameters

For any potential which may be expressed in the form (2), i.e., as a series in the spherical harmonics, the crystal-field parameters b_{lm} in the effective Hamiltonian (1) may be simply obtained by requiring that matrix elements of (2) in the space of the $4f$ functions ψ_{4f},

$$\psi_{4f} = R_{4f}(r) Y_{3m}(\vartheta,\varphi), \quad m = -3, -2, \ldots, 3$$

are equal to matrix elements of (1) in the space of the ket vectors $|3m\rangle$. As a result we obtain

$$b_{lm} = \frac{\beta_{lm}}{\alpha_l} \int_0^{+\infty} R_{4f}^2(r) V_{lm}(r) r^2 dr, \tag{4}$$

where α_l are the Stevens factors and β_{lm} are parameters related to $Y_{lm} \rightarrow \hat{O}_{lm}$ conversion. Both α_l and β_{lm} are tabulated, e.g., in the book of Abragam and Bleaney.[22] $V_{lm}(r)$ is the lm component of the potential. Relation (4) forms the basis of our calculations and we discuss it therefore in some detail.

We recall first that the calculations of the electronic structure using the local spin density functional methods give, as a rule, a good approximation for the distribution of the total electron density in the ground state. As a consequence, the Coulomb potential obtained from this distribution should also be approximately correct. Therefore if we insert in (4) the lm components of V_{Coul}, correct contributions of the Coulomb potential to the CFP's are obtained. A more complex situation occurs if we insert in (4) the components of the total potential—it is well known that the exchange-correlation part of the total potential differs from the correct one-electron exchange-correlation potential and therefore the CFP's obtained with the total potential must be taken with some reserve. Nevertheless we feel that the inclusion of the exchange-correlation potential is a step in the right direction and that b_{lm} calculated from (4) with the lm component of the total instead of Coulomb potential should better reflect the real situation. In what follows the calculations using V_{Coul} and V_{tot} are compared.

The other important point in (4) concerns the $4f$ electron density. While the total electron density is usually well reproduced by the local spin density functional (LSDF) calculation, this does not apply to the single electron densities. Rather than taking the $4f$ electron density from our band calculation we therefore performed separate atomic calculations of the electron structure of isolated rare earths. In these calculations the correction for the self-interaction was included,[23] which assures that the single electron densities are well approximated. Two different valence states of the rare earth were considered—neutral atom and trivalent cation, as we believe that these states represent limits for an actual valence state of the rare earth in the $R\mathrm{Ni}_5$ compounds.

In the FLAPW method the expansion (2) holds automatically only within the atomic spheres. In the previous calculations[16–18] based on the FLAPW method the upper limit of the integration in (4) was therefore taken to be equal to the atomic sphere radius of the R ion. As shown in the next part, an important contribution to CFP's arises from the region outside the atomic sphere, however. In order to increase the integration region we used the least squares method to find the expansion coefficients V_{lm} in (2) also in the region beyond the R ion atomic sphere.

III. RESULTS AND DISCUSSION

The band calculations were performed for the experimental values of $R\mathrm{Ni}_5$ lattice parameters as given by Barthem.[24] For the valence (semicore) states the eigenvalue problem was solved in 84 (28) k points in the irreducible wedge of the Brillouin zone. The radius of the Ni atomic sphere was chosen to be 2.203 a.u. Radii of the R atomic spheres were then chosen to be maximal, compatible with this value and with the requirement of nonoverlapping R and Ni spheres.

The crystal-field parameters were determined using relation (4). As indicated in Sec. II B, four sets of CFP's were calculated. They correspond to two alternative choices of the potential (total and Coulomb potential) and to two different $4f$ electron densities (calculated for the neutral atom and for the R^{3+} ion, both with the self-interaction correction included).

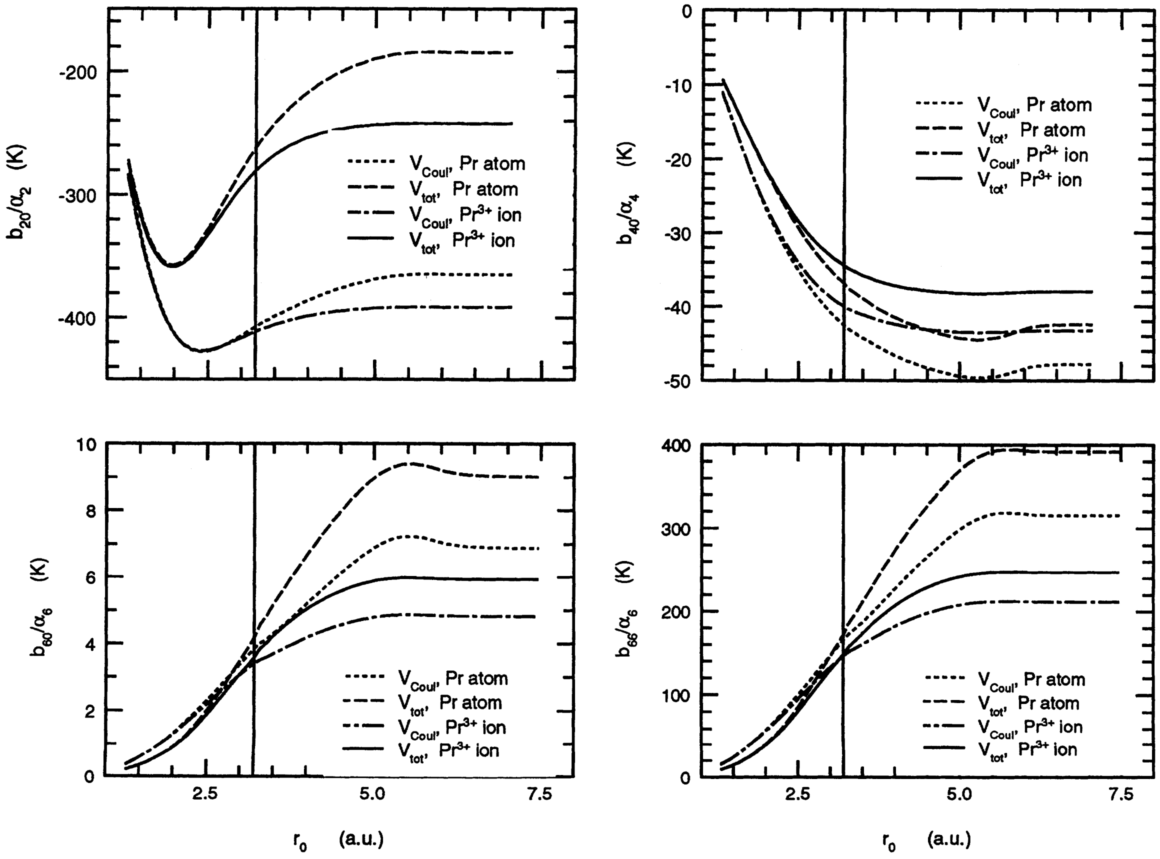

FIG. 1. PrNi_5. Dependence of the crystal-field parameters of praseodymium on the upper integration limit in formula (4). The vertical line corresponds to the radius of the praseodymium atomic sphere. Four sets of calculated parameters correspond to two choices of the potential (total and Coulomb) and two choices of the $4f$ electron density (R atom, R^{3+} ion) in (4).

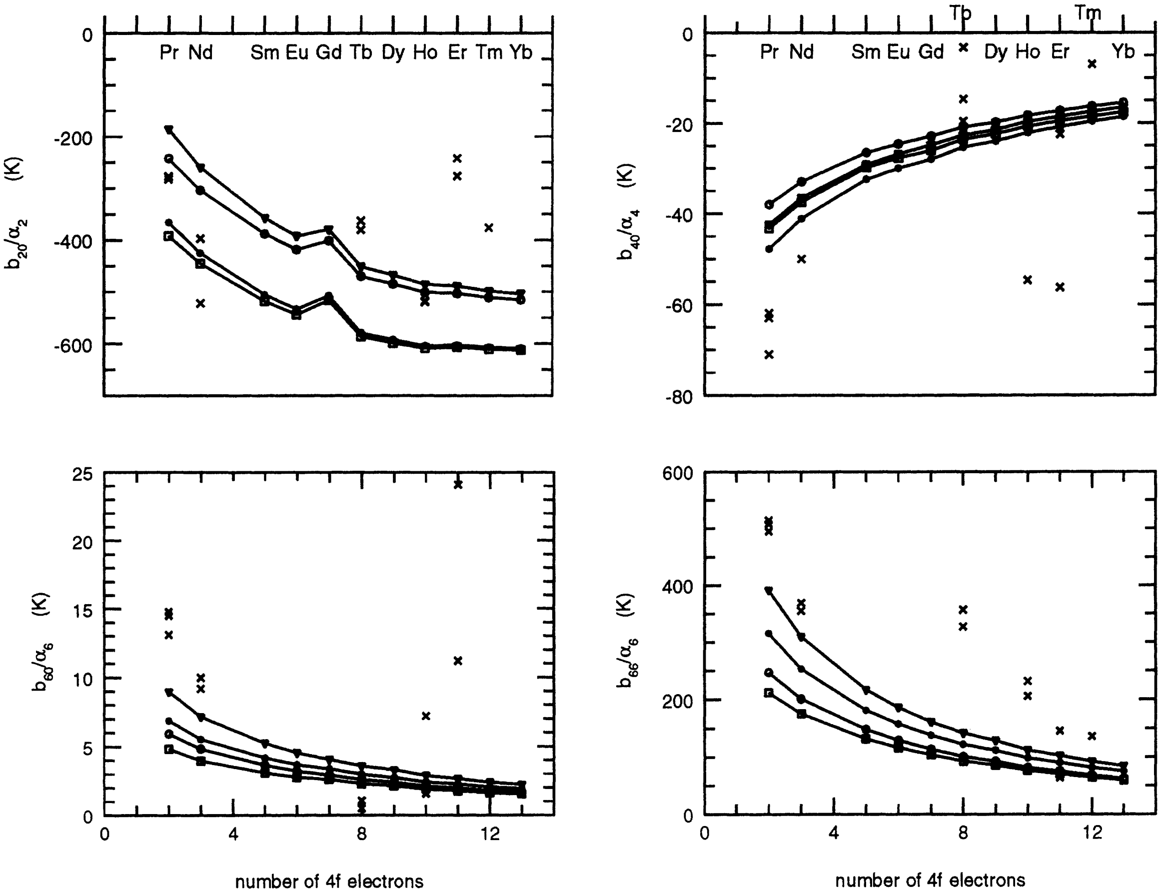

FIG. 2. Crystal-field parameters of rare-earth ions in $R\text{Ni}_5$ system. The values deduced from experiments (×) are taken from Table I. Four sets of calculated parameters correspond to taking in formula (4) V_{tot}, R_{4f} of R^{3+} ion (○); V_{tot}, R_{4f} of R atom (□); V_{Coul}, R_{4f} of R^{3+} ion (▽); and V_{Coul}, R_{4f} of R atom (●).

An important point concerns the upper integration limit in (4). We found that in order to get a reliable value of the integral it must be taken considerably larger than the radius of the R atomic sphere. In Fig. 1 we display as an example the CFP's of praseodymium in PrNi_5 as functions of the upper integration limit (denoted r_0).

In Fig. 2 calculated CFP's for the $R\text{Ni}_5$ systems are shown and compared with the experimental data taken from Table I. It is seen that—with a few exceptions—the calculated CFP's have the same sign and magnitude as CFP's deduced from experiments. With regard to the scatter of CFP's determined from experiment the exceptions are likely to be connected with the uncertainties of the analysis of experimental data as mentioned in Sec. I. Particularly gratifying is the case of PrNi_5 where (i) experimentally determined CFP's are very reliable and (ii) calculated CFP's are not far from their experimental counterparts.

There are clear trends for our CFP's as functions of the rare-earth atom. Due to rather large scatter of the CFP's deduced from various experiments, little can be said, however, as to which extent these trends are real (an agreement obtained for b_{66} might be fortuitous).

For several $R\text{Ni}_5$ compounds (R = Pr, Tb, Dy) we have checked carefully to which extent the resulting CFP's are influenced by the computational method used. In particular the effect of the number of k points in the Brillouin zone, the form of the exchange-correlation potential, and the effect of magnetic ordering on CFP's were studied. None of these three aspects qualitatively change our results, though in separate cases the values of CFP's may change by as much as 40%.[17,18,25]

We regard the neglect of the $4f$ hybridization as the most serious shortcoming of our calculations—this will influence the CFP's in two ways. First, the radial part of the $4f$ wave function, which enters (4), will be modified. Second, due to the various degrees of hybridization for separate $4f$ states, hybridization will contribute to CFP's in a way which cannot be described by our method. As pointed out by Wills and Cooper,[26] if the effect of hybridization on CFP's is considered, it is necessary to take explicitly into account also the electron-electron correlation. This, however, is a nontrivial task which lies beyond the scope of the present paper.

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[1] V. M. T. S. Barthem, D. Gignoux, A. Nait-Saada, and D. Schmitt, Phys. Rev. B **37**, 1733 (1988).

[2] P. A. Algarabel, L. Morellon, M. R. Ibarra, D. Schmitt, D. Gignoux, and A. Tari, J. Appl. Phys. **73**, 6054 (1993).

[3] M. Reiffers, Yu. G. Naidyuk, A. G. M. Jansen, P. Wyder, and I. K. Yanson, Phys. Rev. Lett. **62**, 1560 (1989).

[4] A. Amato, W. Bührer, A. Grayevsky, F. N. Gygax, A. Furrer, N. Kaplan, and A. Schenck, Solid State Commun. **82**, 767 (1992).

[5] V. M. T. S. Barthem, D. Gignoux, A. Nait-Saada, D. Schmitt, and A. Y. Takeuchi, J. Magn. Magn. Mater. **80**, 142 (1989).

[6] E. A. Goremychkin, E. Muhle, I. Natkaniec, M. Popescu, and O. D. Chistyakov, Fiz. Tverd. Tela (Leningrad) **27**, 1989 (1985) [Sov. Phys. Solid State **27**, 1195 (1985)].

[7] A. Nait-Saada, Ph.D. thesis, Grenoble University, 1980.

[8] D. Gignoux, A. Nait-Saada, and R. Perrier de la Bathie, J. Phys. (Paris) Colloq. **40**, C5-188 (1979).

[9] E. A. Goremychkin, E. Muhle, P. G. Ivanitskii, V. T. Korotenko, M. V. Pasechnik, V. V. Slisenko, A. A. Vasilkevich, B. Lippold, O. D. Chistyakov, and E. M. Savitskii, Phys. Status Solidi B **121**, 623 (1984).

[10] D. Gigneaux and J. J. Rhyne, J. Phys. (Paris) Colloq. Suppl. **5**, C5-188 (1979).

[11] E. A. Goremychkin, E. Mühle, B Lippold, O. D. Chistyakov, and E. M. Savitskii, Phys. Status Solidi B **127**, 371 (1985).

[12] R. J. Radvanski, J. J. M. Franse, D. Gignoux, F. E. Keyzel, C. Marquina, and A. Szewczyk, Physica B **177**, 291 (1992).

[13] P. Escudier, D. Gignaux, D. Givord, R. Lemaire, and A. P. Murani, Physica B **86&88**, 197 (1977).

[14] V. M. T. S. Barthem, D. Gignoux, D. Schmitt, and G. Creuzet, J. Magn. Magn. Mater. **78**, 56 (1989).

[15] R. Coehoorn, J. Magn. Magn. Mater. **99**, 55 (1991).

[16] G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, J. Magn. Magn. Mater. **104-105**, 737 (1992).

[17] P. Novák and J. Kuriplach, J. Magn. Magn. Mater. **104-105**, 1499 (1992).

[18] P. Novák and J. Kuriplach, IEEE Trans. Magn. (to be published).

[19] M. Richter, P. M. Oppeneer, H. Eschrig, and B. Johansson, Phys. Rev. B **46**, 13 919 (1992).

[20] P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 339 (1990).

[21] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[22] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970).

[23] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[24] V. Barthem, Ph.D. thesis, Grenoble University, 1987.

[25] J. Kuriplach, Ph.D. thesis, Charles University, Prague, 1994.

[26] J. M. Wills and B. R. Cooper, Phys. Rev. B **36**, 3809 (1987).