PHYSICAL REVIEW B VOLUME 44, NUMBER 10 1 SEPTEMBER 1991-II

Crystal-field effect for the lanthanide-ion series in metallic copper

E. A. Albanesi* and M. C. G. Passeggi
Instituto de Desarrollo Tecnológico para la Industria Quiímica (INTEC), Guemes 3450, 3000 Sante Fe, Argentina

H. M. Pastawski†
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 26 November 1990)

A calculation of the C_4 and C_6 crystal-field parameters for lanthanide ions in metallic copper is presented. It is based on a rigid-band scheme in which the $4f$ impurities are assumed to be immersed in the sea of conduction electrons, with the band states obtained from an augmented-plane-wave calculation. The results show that the crystal-field effects depend mainly on the number and character of band electrons, and can be understood in terms of d-s-band-state hybridization around the Fermi energy of the metal host. Our results on the heavy lanthanides, having the correct signs in all cases, are in reasonable agreement for the C_4 coefficient, while the C_6 coefficients are smaller than those given by experiment. In the case of the light lanthanides, for which no experimental information appears to be available, our results can be considered predictive.

I. INTRODUCTION

Much attention has been focused recently on the studies of $4f$ impurities in metals from the point of view of understanding of magnetic properties and crystalline electric fields in these systems.[1,2]

The crystalline electric field acting on rare-earth (RE) ions diluted in a metallic host plays an essential role in the magnetic properties of these systems. Apart from its direct influence on the magnetization, it is responsible for effects such as magnetocrystalline anisotropy and magnetostriction. These seem to be the main motivation for the large amount of experimental investigation of the crystal-field (CF) splitting in RE ions in metals and intermetallic compounds.[1] Most of the usual spectroscopic techniques have been employed to determine the crystal-field parameters (CFP's) in these systems with the net result that some confusion has arisen about both the signs and magnitudes of the fourth- and sixth-order CFP's.[3] A second motivation concerns itself with the understanding of the microscopic mechanisms governing CF effects of RE ions in metallic hosts.

Phenomenologically the problem is usually described in terms of an effective Hamiltonian, which makes full use of the spatial symmetry of the lattice surrounding the RE ion. For cubic crystal fields the typical starting point is the theory of Lea, Leask, and Wolf[4] giving diagrams for the energy levels as functions of the CFP's, for all J manifolds that appear in the RE series. Recently, Bleaney[5] introduced an approach to this theory in which all the energy levels are given by algebraic expressions, these formulas being especially useful when several levels lie close together. This well-established phenomenological approach allows us to describe the ordering of energy levels and consequently to understand physical properties such as specific heat and magnetical behavior, and thus is particularly adequate to deal with experimental results in a systematic way.

On the other hand, to describe how the CFP's are built up by the intervening physical mechanisms is a difficult task. The simplest scheme, the point-charge model (PCM), is unable to reproduce the experimental sign of the fourth-order CFP. The inclusion of the screening effect of the conduction electrons in the models, as well in the PCM (Refs. 6 and 7) as in more elaborate many-electron theories,[8(a)] also seems insufficient to explain the experiments, although some progress has been obtained combining the screening mechanism[8(b)] with the presence of a $5d$ virtual bond state on the RE ion site interacting with the magnetic $4f$ electrons.[9,10] In considering intermetallic systems, the general conclusion is also that conduction electrons play an essential role in the description of the CF effect and magnetic properties, although these cannot be explained within a free-electronlike model.[2,11–13] Thus a more detailed description of conduction electrons seems to be required.[14]

The impurity problem, although apparently simple, is not easy to describe in a tractable way maintaining the model as reasonably representative of the real system. The main difficulty is that the proper inclusion of the Coulomb repulsion between electrons for important correlation effects should be incorporated. In the present status of the physical models this appears to be a source of difficulty in trying to establish the physics from experiments that can be performed on these systems, (see examples in Refs. 2 and 15). However, two first-principles models of the dilute problem have recently been presented by Dixon and Wardlaw[16] and by Albanesi, Pastawski, and Passeggi,[14] which appear to provide a step forward in the understanding of the origin of crystal fields in metallic systems. While in the former emphasis is placed on the effects of the impurity potential on band states as well as on a proper description of the screening effects of metal electrons, in our case we have dealt directly with the interaction between the $4f$ impurity electrons and the band electrons. Below we comment on how the common features involved in both of these approaches can be reconciled.

In this paper we extend the use of our rigid-band model[14] into a full calculation scheme to obtain the contribution of the interelectronic interaction between the $4f$ and band electrons including all $\mathbf{k}n$ points by an adequate partitioning of the Fermi sphere (FS). This is required in order to get a scheme that allows us to extend the use of the model for predictive purposes. In this respect, a considerable amount of experimental and some physical information is available concerning the CFP of heavy lanthanide ions in noble-metal silver and gold, and to a much lesser extent in copper. No measurements appear to have been made, however, on the light lanthanides in noble metals. For these ions in gold, estimates have been made of the CF splitting and, hence, of the CFP's and the ground states, to study their magnetic properties. This treatment, although useful, must be regarded with caution, since the given mean value for the CFP's does not necessarily incorporate the particular aspects of each RE.[5(a)] In Sec. II we give a brief account of the formalism used to obtain the CFP. In our model, no adjustable parameter is required, and this allows us to understand the role that different mechanisms play in the CF effect for all RE series. We analyze these in Sec. III, where the main features of the model are discussed. We also indicate how it can be used in a more simple—but still accurate—way. This will be useful as a complement in experimental works. We find parameters with the correct signs and order of magnitude, which result from a balance between the different contributions of the filled bands. The systematic agreement with experiment provides additional support for the idea that effects in metals are determined to a large extent by the electronic structure of the metal host. The results are summarized in Sec. IV, and the main consequences of our model are discussed.

II. THE MODEL: DESCRIPTION AND COMPUTATIONAL DETAILS

The model takes into consideration that the metal electrons penetrate the ion and interact with the electrons in the f-shell magnetic orbitals, and that it requires a detailed description of the conduction electrons of the metal. The magnetic multiplet state $|4f\,JM\rangle$ of the impurity is assumed to be immersed in the sea of conduction electrons that are described by the same states as in the pure host. This scheme can be regarded as a zeroth-order approximation in the charge self-consistency at the impurity site. In this simple model we obtain the CF effects on the $4f$ shell of the impurity RE ion from the direct and exchange Coulomb interaction with the conduction electrons treated perturbatively at first order. The band states have been obtained with an augmented-plane-wave (APW) method, along the lines given by Burdick.[17] It is known that the Chodorow potential used here gives a notably good description of bands for Cu, in particular for the bottom of the sp band, and a rather good description of the d bands and its widths, in comparison with experiment.[18,19] In the APW scheme the band states are given as linear combinations [with coefficients $d_{\lambda\mu}(\mathbf{k},n)$] of spherical harmonics $Y_{\lambda\mu}(\hat{\mathbf{r}})$, which inside the muffin-tin sphere are of the form

$$|\mathbf{k}n\sigma''\rangle=\sum_{\lambda,\mu} d_{\lambda\mu}(\mathbf{k},n)\mathcal{R}_{\lambda}(n,r)Y_{\lambda\mu}(\hat{\mathbf{r}})|\sigma''\rangle\ . \tag{1}$$

Here $\mathcal{R}_{\lambda}(n,r)$ is the radial APW function, $|\sigma''\rangle$ is the spin state, and λ,λ' refers to the $s,p,d,\ldots$ components of the APW band states of Cu.

Within a given $|JM\rangle$ multiplet, the phenomenological effective operator in cubic symmetry can be written as

$$\begin{aligned}\hat{\mathcal{H}}(\hat{J})=b_4^0[O_4^0(\hat{J})+\sqrt{5/4}[O_4^4(\hat{J})+O_4^{-4}(\hat{J})]\\ +b_6^0[O_6^0(\hat{J})-\sqrt{7/2}[O_6^4(\hat{J})+O_6^{-4}(\hat{J})]\ ,\end{aligned} \tag{2}$$

where the $O_K^Q(\hat{J})$ are the Smith and Thornley operators and b_K^0 are the CFP's. In our model, a first-order calculation of the interaction between determinant states of the type $|\{\mathbf{k}n\}f^nLSJM\rangle$, with $\{\mathbf{k}n\}$ representing the set of band states occupied up to the Fermi energy (ε_F), produce, after some algebra, the fourth- b_4^0 and sixth-b_6^0 order parameters as

$$b_K^{0(\mathrm{cond})}=2^K(2J+1)\left[\frac{(2J-K)!}{(2J+K+1)!}\right]^{1/2}(-1)^{L+S+J+K}(2K+1)^{1/2}\begin{Bmatrix} S & J & L\\ K & L & J\end{Bmatrix}\langle f^nLS\|u^{(K)}\|f^nLS\rangle t^{(K)} \tag{3}$$

with

$$t^{(K)}=\sum_m(-1)^{l-m}\begin{bmatrix} l & l & K\\ m & -m & 0\end{bmatrix}\sum_{\substack{\mathbf{k}n\sigma''\\ (\mathrm{occ.})}} g_{m_\uparrow m_\uparrow}^{(\mathbf{k}n\sigma'')}\ . \tag{4}$$

The coefficients $\langle f^nLS\|u^{(K)}\|f^nLS\rangle$ are tabulated by Nielson and Koster,[20] and the $g_{m_\uparrow m_\uparrow}^{(\mathbf{k}n\sigma'')}$ represent the direct and exchange Coulomb interaction between the $4f$ magnetic electrons and the band electrons from the metal host, in terms of the $F_{\lambda\lambda'}^K$ and $G_{\lambda\lambda'}^{\mathcal{L}}$ Slater's direct and exchange integrals.[14] These integrals were calculated using accurate numerical relativistic Hartree-Fock self-consistent field $4f$ function for the RE ions.[21] This function has not been reported for yterbium, and we have not attempted to replace it by one obtained from a different calculation in order to avoid altering the systematic of our results. Also we have not considered the cerium, since it is known that this ion has a notorious tendency to show mixed valence behavior. It must be noted that the

$4f$ functions are orthogonal to all APW functions other than those with $\lambda=3$ (f, components) owing to the orthogonality between the corresponding spherical harmonics. Band states with f components contain only a small amount of charge and thus nonorthogonality effects can be neglected. It can be seen that $t^{(K)}$ depend on the filling scheme of the band states up to the Fermi level, but contain angular factors only related (and summed up) to the $4f$ shell functions, being independent on L, S, and J quantum numbers. b_K^0 contain the complete dependence on these quantum numbers through the angular factors other than those included in $t^{(K)}$ as they appear in Eq. (3). From the point of view of the formalism, these have the advantage that they can be derived by the use of formal group theory.[22] However, the signs of the b_K parameters do not present a convenient systematic in going over the RE series. In order to present our results using another set of CFP's, the Hamiltonian of Eq. (1) can also be written using Stevens' operators[23] $\mathcal{S}_K^Q(\hat{J})$ as

$$\hat{\mathcal{H}}(\hat{J})=C_4^0\beta_J[\mathcal{S}_4^0(\hat{J})+5\mathcal{S}_6^4(\hat{J})] + C_6^0\gamma_J[\mathcal{S}_6^0(\hat{J})+21\mathcal{S}_6^6(\hat{J})] \ . \tag{5}$$

The constants β_J and γ_J arise from the matrix elements within a given J manifold and were tabulated by Hutchings[24] for all RE ions. Omitting the superscript zero for the fourth- and sixth-order parameters, the relationship between the two sets of parameters is given by

$$C_4=b_4/8\beta_J \quad \text{and} \quad C_6=b_6/16\gamma_J \ . \tag{6}$$

The C_K's, although originally associated with the PCM, are another set of parameters frequently used to describe the crystal-field effect. They have lost the multiplicative factors β_J and γ_J contained in b_4 and b_6, respectively, resulting systematically, for the systems of our interest, in $C_4<0$ and $C_6>0$. Thus we prefer this set of CFP's to present our results.

The evaluation of $t^{(K)}$ [Eq. (4)] requires us to consider a sum over the states within the Fermi sphere (FS). This means that after obtaining the APW states at each $\mathbf{k}$ within the first Brillouin zone (BZ), direct and exchange contributions must be evaluated. This causes a dependence on $\mathbf{k}$ vectors and eigenstates through the $F_{\lambda\lambda'}^K$ and $G_{\lambda\lambda'}^{\mathcal{L}}$ integrals. Also, it must be noted that it is not possible to factor out the Slater's integrals in terms of the density of states if all contributions from different $\lambda\lambda'$ are to be retained. We studied this dependence in detail for some $\mathbf{k}$ points, showing[14] that the relevance of the model lies in the description of the energy-band crossover region around the Fermi energy ε_F, where band hybridization take place. Thus, we have made a thorough sampling of the FS in about ±20% around ε_F. This requires us to make the sampling as complete as possible considering that each $|\mathbf{k}n\rangle$ band state has a weight that represents the volume of the BZ associated to it, in order to account for the details of the Fermi-sphere filling. We have used the weights provided by the partition given by Burdick, where the first BZ is partitioned into 2048 cubical volume elements.

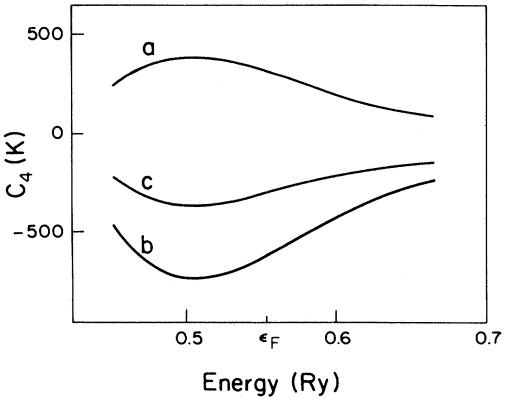

FIG. 1. The C_4 parameter for Tm as a function of energy. Curve (a) direct contribution; curve (b) exchange contribution; curve (c) total parameter.

III. DISCUSSION OF RESULTS

By studying the direct and exchange contribution to C_4 parameters as a function of energy, it is observed that their plots against energy show results with opposite signs, which are rather symmetrical. In Fig. 1 we show this behavior exemplifying the case of Tm. The plot corresponds to averaged curves calculated at each particular energy without considering the weight of the BZ associated to that point. The exchange contribution, however, dominates the direct one, resulting finally in a total parameter that resembles the shape of this contribution. For C_6 the curves corresponding to direct and exchange contributions behave similarly, having the results that for this parameter the importance of the exchange term is enhanced, since it is responsible for the main features of the total sixth-order parameter. The importance of the exchange term has been recognized previously by other CF model system calculations.[10,11]

Consistent with the APW charge density distribution, our calculations show that the more important contributions correspond to the diagonal terms in which $\lambda=\lambda'=2$ and to a lesser extent to those in which at least one or both λ (λ') $=2$. This means that the hybridization is a significant contributory source. The diagonal term $\lambda=2$ is present in the low-order parameter C_4, and our first-order perturbative calculation gives satisfactory results for all RE series. For the higher-order C_6 parameter, selection rules of the $3j$ factors of Eq. (2) allow only a diagonal term for $\lambda\geq 3$. Under these conditions the sixth-order parameter could be nonzero only if the f-band states ($\lambda=3$) have a significant amount of charge, which is not the case for pure Cu and Ag. As band states with f components contain, however, a very small amount of charge, the nonorthogonality effects between band states with $\lambda=3$ and the $4f$ functions can be ignored. Thus, within the features of our model it turns out that hybridization is responsible for a nonvanishing value of the sixth-order parameter. In Fig. 2 we plot the total and diagonal C_6 parameter for Tm to show this fact.

In Figs. 3 and 4 we plotted the total "summed" C_4 and C_6 CFP's, respectively, versus energy. Summed means

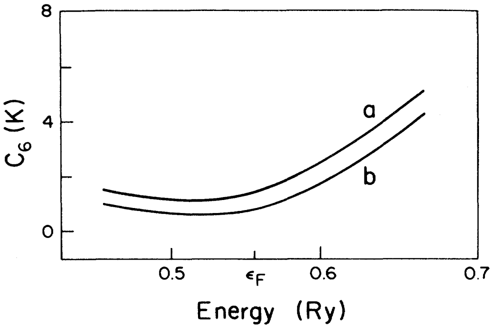

FIG. 2. The C_6 parameter for Tm as a function of energy; curve (a) total parameter; curve (b) diagonal contribution.

that to each energy value abscissa, the CFP is obtained by adding all contributions from any of the previous $\mathbf{k}n$ that lie in that region. The theoretical value that is compared with experiment is that obtained when the sum is performed over all occupied states, that is, up to ε_F. For metallic Cu, it can be seen that below ε_F lie the five $3d$ band states fully occupied, and the $4s$ band half occupied.[14] This is the crossover energy region where an important hybridization of the bands takes place. The band that emerges above ε_F is also hybridized, although it has mainly an s character, which increases with energy. Our calculation for lanthanide impurities shows that the CF effect depends mainly on the number and character of band electrons, resulting in parameters with the correct signs from a balance between the different contribution of the filled bands.

Figure 3 shows the systematic followed by the C_4 parameters. We see two close but separate branches: one for the heavy RE (Tm,Er,Ho,Dy) and the other for Tb and the light lanthanides (Sm,Pm,Nd,Pr). The model predicts that for the same metallic host the CFP lightly increases in magnitude in going from the heavier to the lighter RE, although this assertion must be understood as a trend, since the model is hardly sensitive enough to distinguish between such small differences. However, the same can be said for the different experimental techniques and the possible choices of sets of CFP's obtained from the data (see examples in Table I and Ref. 5). The particular aspects of each impurity go into the model mainly through the radial function, which enters into the $F^{K}_{\lambda\lambda'}$ and $G^{\mathcal{L}}_{\lambda\lambda'}$ Slater's integrals. Although small, the differences in those functions appear to be significant, precluding us from obtaining a universal curve for a given metal host. The sixth- and fourth-order CFP's for Eu, Gd, and Lu and the sixth-order CFP for Sm are zero to first order in J owing to the angular factors provided by matrix elements within the ground manifold J. For these ions only higher-order contributions could cause some effect. To maintain the effective Hamiltonian described within the ground multiplet, a perturbative description[25] could be adopted to include the excited low-lying $|J'M'\rangle$ manifolds.

In Fig. 4 we show the systematic followed by the C_6 parameter. We see that except for praseodymium, the trend is that the parameter is increased in going from the heavier to the lighter RE, although around ε_F the model allows us to distinguish between two values, 0.6 K for Pr and Nd, and 0.3 K for the heavy ions. These results are in accordance with the experimental trend, although ours are an order of magnitude smaller. C_6 is made up from the addition of only small terms, which causes the chances of adjusting the magnitude of this parameter closely to become difficult. The praseodymium ion shows an unusually small C_6 parameter of 0.01 K. Small differences in the $F^{\mathcal{K}}_{\lambda\lambda'}$ and $G^{\mathcal{L}}_{\lambda\lambda'}$ owing to $4f$ radial functions of the RE ion, that are a little different, could cause this effect in performing the sum over $\mathbf{k}n$, which Eq. (3) prescribes. Second-order effects in $\{\mathbf{k}'n'\}$ could be important for Pm. In maintaining the first-order scheme in the ground manifold J, a second-order effect on the filling scheme of the band states of the metal host might become important. However, it seems that a perturbative treatment of mixing $\mathbf{k},\mathbf{k}'$ band states maintaining the rigid-band model could be not adequate owing to the small value of C_6. Under these circumstances it would be necessary to consider a scheme where the impurity potentials have been included properly so as to modify the band states and perhaps to go into second order in J', since for samarium this last effect could be important.[5] In Table I we compare our summed predictive calculations for Cu with the available experimental information

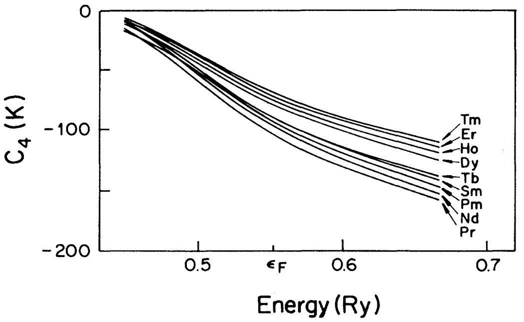

FIG. 3. Summed C_4 CFP's as a function of energy for the lanthanide series. The theoretical values shown in Table I are those corresponding to ε_F.

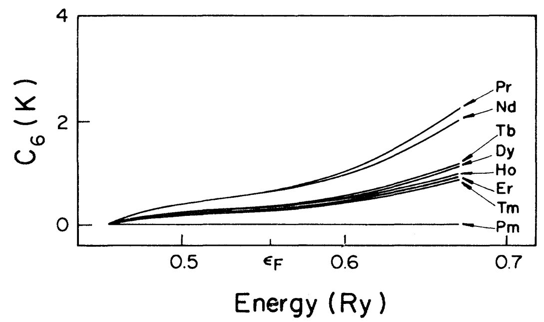

FIG. 4. Summed C_6 CFP's as a function of energy for the lanthanide series. The theoretical values shown in Table I are those corresponding to ε_F.

TABLE I. Summed CFP's up to ε_F (see text), as compared with measurements available for different noble metals. The dispersion existing in the experimental results for noble metals from different authors, is discussed in Refs. 5 and 14.

	Experiment			This work	
System	C_4 (K)	C_6 (K)	Reference	C_4 (K)	C_6 (K)
Au:Tm	-17	2	9		
	-12	1	5(a)		
Ag:Tm	-30	5.5	9		
	-6	6.5	26		
Cu:Tm				-71.8	0.26
Au:Er	-33	6.5	9		
	-29.7	5.6	27		
Ag:Er	-70	13	9		
Cu:Er				-74.3	0.28
Au:Ho	-20	4	28		
	-33	2.7	5(a)		
Ag:Ho	-70	13	9		
Cu:Ho				-77.0	0.30
Au:Dy	-30	6	28		
	-25.4	1.3	29(a)		
	-35.9	1.6	30		
Ag:Dy	-70	13	9		
	-68.7	15.1	31		
	-13.5	5.7	29(b)		
Cu:Dy				-79.8	0.32
Ag:Tb	-70	13	9		
Cu:Tb				-93.7	0.34
Cu:Sm				-92.0	
Cu:Pm				-95.4	0.01
Cu:Nd				-98.8	0.54
Cu:Pr				-102.6	0.62

obtained in different noble metals, since in these cases one expects CFP that would be similar in sign and magnitude to those in Cu. The experimental trend suggests that parameters decrease in magnitude when going from Cu to Au. Our results seem to be in accordance with this trend, since our calculated values in Cu are systematically higher than those measured in Ag and Au.

As the d-s balance is modified by increasing the s character for energies above ε_F, one should expect some differences to appear in the CFP's in this energy region. These states could become occupied through changes in the number of conduction electrons, i.e., by changing the concentration of impurities or by doping the system in a range in which the crystal structure is preserved. From Figs. 3 and 4 it is seen that the curves corresponding to CFP's are not strongly affected in this region around ε_F where the model maintains its significance. This is expected for the C_4 parameter, since the d-d diagonal term is always the dominant contribution. For C_6, owing to selection rules, there is no diagonal contribution except whenever f-band states are present, which is not the case for Cu. Because of this, one might expect that more noticeable variations of C_6 could be obtained. However, our calculation shows that the changes in the d-s balance are not enough to produce them. A more drastic reduction in the ratio of d-s states would be necessary, as is the case for cubic intermetallic compound RE noble metals, where this ratio is 4:1.[11(a),13] This is a fair amount lower than that obtained with our model for impurities. It is known that in intermetallic compounds the CF's are different, and, although the CFP's maintain their magnitudes, C_6 changes its sign.

The partition of the BZ that we have used in order to sum in $\mathbf{k}n$, demands some computational effort. However, our calculations show that it is possible to use our model in a less costly form as an approximation, calculating the CFF's in the region of about $\pm 20\%$ of ε_F for any relatively close grid in energy, without any further sum. Taking the averaged curve from this value, the C_4 parameter results in correct signs, and although their magnitudes are somewhat overvalued, it is possible to understand qualitatively the CF effect in the same way as discussed before. The use of this procedure might be very convenient as an orientation in experimental works on systems for which no measurements or calculations have been made before.

IV. CONCLUSIONS

We have performed a calculation for the C_4 and C_6 CFP's of lanthanide impurities in copper. The usual idea, which proposes a $5d$ virtual state localized around the RE, could be justified by our model in terms of electrons of d character (distributed between e_g and t_{2g} symmetries), which are naturally provided through the band calculation. Also the hybridization of the bands could be assimilated with the idea of screening. We have shown that the CF effect can be understood in terms of the hybridization of $3d$ and $4s$ bands around ε_F. Moreover, C_6 would vanish otherwise. The Coulomb interaction between $4f$ and band-state electrons must include both the direct and exchange terms. The trend that our results predict is that for a given metallic host the fourth-order CFP lightly increases in magnitude in going from the heavier to the lighter RE. In summary, our model calculation reveals that as long as the host provides d-band states where the filling scheme up to ε_F and d-s hybridization is properly included, an acceptable zeroth-order approximation is given to account for the magnitude and sign of C_4, irrespective of the effects that should arise on the band states by the presence of modified potential at the impurity site. In the case of intermetallic compounds of the type RE-NM, where NM=Cu,Ag,Au, irregularities in the intervening potentials are not present as compared with the impurity problem. Thus one may think the model would be intuitively better adjusted for this case, since the self-consistent potential automatically includes the presence of the RE ions.

The first-order perturbative scheme in J seems adequate in all cases. Naturally for both parameters on Eu, Gd, and Lu and for C_6 on Sm in which angular factors arising from matrix elements within the ground manifold J are zero, only higher-order effects could eventually make contributions. The C_6 parameter increases in going from the heavier to the lighter RE, except for Pm, which shows an unusually small value. For this parameter, as for samarium, second-order effects in $|\mathbf{k}'n'\rangle$ could be important, and a second-order perturbation description on the excited low-lying $|J'M'\rangle$ manifolds could be adopted. The impurity contributes through the angular coefficients determined for the $J(L,S)$ multiplet and through the radial $4f$ wave function in the Slater's integrals $F^{K}_{\lambda\lambda'}$ and $G^{\mathcal{L}}_{\lambda\lambda'}$, although our calculation shows that the CF effects depend mainly on the number and character of band electrons, resulting in parameters with the correct signs. Thus, by changing the RE, and since no adjustable parameter is required, the model seems adequate for the study of the CFP's. This should be particularly important, since, at present, no measurements appear to have been made on the light lanthanides in noble metals.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Consejo Nacional de Investigaciones Científicas y Ténicas (CONICET), Argentina, through Grant No. PID 75300. One of us (E.A.A.) also acknowledges the Facultad de Ingeniería (UNER), where part of this work was done.

---

[*] Also at Facultad de Ingeniería (Bioingeniería), Universidad Nacional de Entre Ríos, 3100 Oro Verde (Paraná), Argentina.

[†] On leave from INTEC (CONICET—UNL), Guemes 3450, 3000 Santa Fe, Argentina.

[1] *Proceedings of the International Crystalline Electric Field Conference IV, International Conference on Crystal Field and Structural Effects in f-Electron Systems*, edited by R. Guertin, W. Suski, and Z. Zolnierek (Plenum, New York, 1982).

[2] B. Frick and M. Loewenhaupt, Z. Phys. B **63**, 213 (1986); **63**, 231 (1986).

[3] B. Barbara, Y. Berthier, R. Devine, and M. Rossignol, J. Phys. F **12**, 2625 (1982).

[4] K. Lea, M. Leask, and W. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[5] (a) B. Bleaney, Proc. R. Soc. London, Ser. A **424**, 289 (1989); (b) **424**, 299 (1989).

[6] J. Duthie and V. Heine, J. Phys. F **9**, 1349 (1979).

[7] A. del Moral, J. Phys. F **14**, 1477 (1984).

[8] (a) F. Christodoulos and J. M. Dixon, J. Phys. C **20**, 5537 (1987); (b) Phys. Lett. A **124**, 437 (1987).

[9] G. Williams and L. Hirst, Phys. Rev. **185**, 407 (1969).

[10] H. Chow, Phys. Rev. B **7**, 3404 (1973).

[11] (a) D. Schmitt, J. Phys. F **9**, 1745 (1979); (b) **9**, 1759 (1979).

[12] M. Belakhovsky and D. Ray, Phys. Rev. B **12**, 3956 (1975).

[13] M. Belakhovsky, J. Pierre, and D. Ray, J. Phys. F **5**, 2274 (1975).

[14] E. A. Albanesi, H. M. Pastawski, and M. C. G. Passeggi, Physica B **154**, 397 (1989). In Eq. (7b) of this reference the last 3-j factor must be read as a 6-j factor given by $\begin{Bmatrix} \lambda & \lambda' & K \\ l & l & \mathcal{L} \end{Bmatrix}$.

[15] P. Kikkert and L. Niesen, Hyperfine Interact. **8**, 135 (1980); J. Phys. F **11**, 547 (1981).

[16] J. M. Dixon and R. Wardlaw, Physica A **135**, 105 (1986); J. Phys. C **19**, 943 (1986).

[17] G. Burdick, Phys. Rev. **129**, 138 (1964).

[18] P. Thiry, D. Chandesris, J. Lecante, C. Guillot, R. Pinchaux, and Y. Petroff, Phys. Rev. Lett. **43**, 82 (1979).

[19] W. Altman, V. Dose, A. Goldman, U. Kolak, and J. Rogozic, Phys. Rev. B **29**, 3015 (1984).

[20] D. Smith and J. Thornley, Proc. Phys. Soc. **89**, 779 (1966).

[21] K. Saxena and G. Malli, Phys. Rev. A **3**, 1278 (1971).

[22] B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).

[23] K. W. H. Stevens, Proc. Phys. Soc. A **65**, 209 (1952).

[24] M. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16.

[25] E. A. Albanesi and M. C. G. Passeggi, Phys. Lett. A **113**, 210 (1985).

[26] K. Post and L. Niesen, J. Phys. F **14**, 2203 (1984).

[27] L. Tao, D. Davidov, R. Orbach, and E. Chock, Phys. Rev. B **4**, 5 (1971).

[28] A. Murani, J. Phys. C **3**, Suppl. (2), S153 (1970).

[29] (a) P. Kikkert and L. Niesen, J. Phys. F **11**, 547 (1981); (b) Phys. Rev. B **23**, 2126 (1981).

[30] W. Wagner, L. Asch, and G. Kalvius, Hyperfine Interact. **4**, 441 (1978).

[31] S. Oseroff, M. Passeggi, D. Wohllenben, and S. Schultz, Phys. Rev. B **15**, 1283 (1977).