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## LETTER TO THE EDITOR

# On the crystal field effect for $\text{Ho}^{3+}$ and $\text{Er}^{3+}$ impurities in metallic copper

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**Abstract.** A calculation of the crystal field parameters for  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  impurities in metallic copper is reported. The results can be understood in terms of the hybridization of d-s band states around the Fermi energy of the metal host. The possibility that the model can be used for the lanthanide series in noble metals, including those for which no experimental information is available, is discussed.

Much attention has been focused recently on the studies of 4f impurities in metals. It is known that a crystalline electric field (CF) acting on rare earth (RE) ions diluted in metallic hosts or in RE-metal glasses, plays an essential role in determining the magnetic properties of these systems [1]. The problem is usually described with the formalism of phenomenological effective Hamiltonians, which make full use of the spatial symmetry of the lattice surrounding the RE ion. For a cubic crystal field the typical starting point is the theory of Lea *et al* [2] giving diagrams for the energy levels as functions of the crystal field parameters (CFP), for all the *J*-manifold that appears in the RE series. Recently, Bleaney [3] gave a new approach to this theory in which all the energy levels are given by algebraic expressions, these formulae being specially 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 magnetic behaviour, and it is, therefore, particularly suitable for dealing with experimental results in a systematic way.

On the other hand, to describe how the CFP are built up by the intervening physical mechanisms is a difficult task [4–7], since the impurity problem, although apparently simple, is not easy to describe in a tractable way while still keeping the model reasonably representative of the real system. The main difficulty is the proper inclusion of the Coulomb repulsion between electrons, since important correlation effects are incorporated. In the present status of the physical models this appears to be a source of difficulty in trying to extract the physics that experiments show about these systems [8, 9]. However, two first-principles models on the dilute problem have been presented recently by Dixon and Wardlaw [10] and by Albanesi *et al* [7], 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 these approaches can be conciliated.

In this letter we extend the use of our rigid band model [7] in a full scheme calculation to obtain the contribution from all  $kn$  points by an adequate partitioning of the Fermi sphere (FS). This is required in order to obtain a scheme which allows us to extend the utility 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 the noble metals silver and gold, and to a 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 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 does not incorporate the particular aspects of each RE [3]. In our model, no adjustable parameter is needed, and this allows us to understand the role that different mechanisms play in the CF effect for all RE series. The number of calculations required for this is considerable and they will be undertaken later. Here, we analyse the case of holmium and erbium impurities in copper, giving the main features of this scheme. We also indicate how it can be used in a more simple—but still accurate—way. This will be useful as a complement to the experimental work.

The model considers that the metal electrons penetrate the ion and interact with the electrons in the f-shell magnetic orbitals, and requires a detailed description of the conduction electrons of the metal. The magnetic multiplet state  $|4f^n JM\rangle$  of the impurity is assumed to be immersed in the sea of conduction electrons which 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. The band states have been obtained using an augmented plane wave method (APW), along the lines given by Burdick [11]. It is known that the Chodorow potential used gives a notably good description of the bands for Cu, in particular for the bottom of the sp band, and a rather good description of the d bands and their width; this is in comparison with other experiments [12, 13].

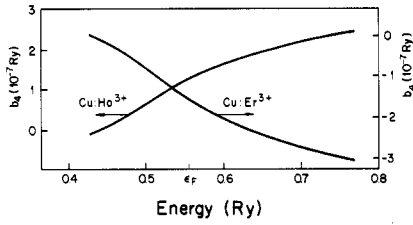
The phenomenological effective operator within a given  $|JM\rangle$  multiplet can be written as

$$\mathcal{H}(\hat{J}) = \sum_{KQ} b_Q^K O_Q^K(\hat{J}) \quad (1)$$

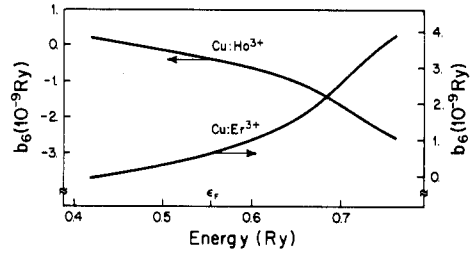
where the  $O_Q^K(\hat{J})$  are the Smith and Thornley operators and the  $b_Q^K$  are the CFP. In our model, a first-order calculation of the  $\mathcal{H}(\hat{J})$  between the determinantal states, after some algebra, produces the  $b_4$  and  $b_6$  fourth- and sixth-order parameters respectively for cubic symmetry. The results are proportional to

$$\sum_{kn\sigma'} g_{m\uparrow m\uparrow}^{(kn\sigma')}$$

where  $g_{m\uparrow m\uparrow}^{(kn\sigma')}$  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 radial integrals respectively, where  $\lambda$  and  $\lambda'$  refer to the s, p, d . . .-like band states of Cu. These integrals were calculated using the accurate numerical relativistic Hartree-Fock self-consistent field 4f function for the RE ion [14]. More details of the model and the computed expressions are given in [7].



**Figure 1.** Summed  $b_4$  CFP as a function of energy. The theoretical values shown in table 1 are those corresponding to  $\epsilon_F$ .



**Figure 2.** Summed  $b_6$  CFP as a function of energy. The theoretical values shown in table 1 are those corresponding to  $\epsilon_F$ .

The evaluation of CFP requires us to consider a sum over the states within the Fermi sphere (FS). This means that after obtaining the APW states for each  $k$ , direct and exchange contributions must be evaluated. This causes a dependence on  $k$  vectors and eigenstates through the  $F_{\lambda\lambda'}^K$  and  $G_{\lambda\lambda'}^L$  integrals. Also, it must be noted that it is not possible to factorize out the Slater integrals in terms of the density of states if all contributions from different  $\lambda\lambda'$  are to be retained. We have studied some  $k$  points in detail for this dependence, showing [7] that the relevance of the model lies in the description of the energy band crossover region around the Fermi energy  $\epsilon_F$ , where band hybridization takes place. Thus, we have made a thorough sampling of  $\pm 20\%$  of the FS around  $\epsilon_F$ . This requires us to make the sampling as complete as possible, considering that each  $kn$  band state has a weight which represents the volume of the Brillouin zone (BZ) associated with it, in order to account for details of the Fermi sphere filling. We have used the partition given by Burdick, where the first BZ is partitioned into 2048 cubical volume elements. By symmetry arguments, it is only necessary to make the computation for 89  $k$  vectors lying in the  $1/48$  of the BZ.

By studying the direct and exchange contribution to both parameters as a function of energy it is observed that their plots against energy show rather symmetrical results with opposite signs. The exchange contribution, however, dominates the direct one, finally resulting in the total parameter giving a plot which resembles it. The importance that the exchange term has in our model is in agreement with previous calculations [15, 16]. Consistently with the APW charge density distribution, our calculations show that the more important contributions correspond to those in which at least one or both of  $\lambda$  and  $\lambda'$  is equal to 2. This means that the hybridization is a significant contributory source. Moreover, it turns out that this is essential in describing the  $b_6$  parameter, as hybridization is responsible for a non-vanishing value when the f bands are not significantly present as is the case for Cu.

In figures 1 and 2 we plotted the total 'summed'  $b_4$  and  $b_6$  CFP respectively against energy. 'Summed' means that at each energy value, the CFP is obtained by including all the  $kn$  that lie in that energy region. The theoretical value that is compared with experiments is the value obtained when the sum is performed over all occupied states, that is, up to  $\epsilon_F$ . For metallic Cu, it can be seen that below  $\epsilon_F$  lie the five 3d band states, fully occupied, and the 4s band, half occupied [7]. This is the crossover energy region where an important hybridization of the bands takes place. The band that emerges above  $\epsilon_F$  is also hybridized, although it has mainly s character, to an extent that increases with energy. Our calculations for some different RE impurities show that the CF effect depends

**Table 1.** Summed CFP for  $\varepsilon_F$  (see text), as compared with measurements available for  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$ . The differences in the experimental results for noble metals from different authors is discussed in [3, 7].

System	Experimental			This work	
	$b_4$ ( $10^{-7}$ Ryd)	$b_6$ ( $10^{-9}$ Ryd)	Reference	$b_4$ ( $10^{-7}$ Ryd)	$b_6$ ( $10^{-9}$ Ryd)
Au: $\text{Ho}^{3+}$	0.34	-0.52	[18]		
Ag: $\text{Ho}^{3+}$	1.18	-1.70	[19]		
Cu: $\text{Ho}^{3+}$				1.30	-0.04
Au: $\text{Er}^{3+}$	-0.74	1.36	[19]		
Ag: $\text{Er}^{3+}$	-1.57	2.73	[19]		
Cu: $\text{Er}^{3+}$				-1.67	0.06

mainly on the number and character of band electrons, resulting in parameters with the right signs from a balance between the different contributions of the filled bands. As the d-s balance is modified, increasing the degree of s character for energies above  $\varepsilon_F$ , one would expect that some differences should appear in the CFP 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 figures 1 and 2 it is seen that the curves corresponding to CFP are not strongly modified in this region around  $\varepsilon_F$  where the model maintains its significance. This result is expected for the  $b_4$  parameter since the d-d diagonal term is always the dominant contribution. For  $b_6$ , owing to selection rules, there are no diagonal contributions except where f-band states are present, which is not the case for Cu, and thus it would be more noticeable if the modification was extended. However, our calculation shows that the changes in the d-s balance are not enough to produce the diagonal contributions. More drastic reduction in the ratio of d-s states would be necessary, as is the case for the cubic intermetallic compounds, RE-noble metal, where the ratio is 4 to 1 [16, 17], which is much lower than that obtained with our model for impurities. It is known that in intermetallic compounds the CF are different and although the CFP maintain their magnitudes  $b_6$  changes its sign. In table 1 we compare our summed predictive calculations for Cu with measurements for different noble metals, since one expects CFP which are similar in sign and order of magnitude. Our results show good accord with the experimental trend. However,  $b_6$  is obtained by summing small terms and is subject to relatively large errors.

The partition of the BZ that we have used in order to sum over  $kn$  demands a considerable computational effort. However, our calculations show that it is possible to use our model in a less expensive form as an approximation, calculating the CFP in the region about  $\pm 20\%$  of  $\varepsilon_F$  for any relatively close grid in energy, without any further summing. Deriving the curve from these values gives parameters with correct signs, and although their magnitudes are somewhat overvalued, it is possible to understand qualitatively the CF effect in the way already described. The use of this procedure might be very convenient for orientation in experimental work on systems for which no measurements or calculations have been made before.

In summary, we have performed a calculation for the  $b_4$  and  $b_6$  CFP of  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  impurities in Cu. The usual idea which proposes a 5d virtual bound 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 reconciled 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  $\varepsilon_F$ . Moreover,  $b_6$  would vanish otherwise. The Coulomb interaction between 4f and band state electrons must include both the direct and the exchange terms. The impurity contributes through the angular coefficients determined for the  $J(L, S)$  multiplet and through the radial 4f wave function in the Slater integrals  $F_{\lambda\lambda}^K$  and  $G_{\lambda\lambda}^{\mathcal{L}}$ . However, our preliminary calculation for some other RE impurities shows that the CF effects depend mainly on the number and character of band electrons, resulting in parameters with the right signs. Thus, on changing the RE and since no adjustable parameter is required, the model seems adequate for the study of the CFP. This should be particularly important since, at present, no measurements appear to have been made on the light lanthanides in noble metals.

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