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Calculated crystal-field parameters for rare-earth impurities in noble metals

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From first-principles density-functional calculations of the charge distribution the crystal-field (CF) parameters for $4f$ states of Er and Dy impurities in Ag and Au have been evaluated. The calculations are based on an optimized linear combination of atomic orbitals scheme, where the local-density approximation (LDA) is used for the conduction-electron states, while the localized rare-earth $4f$ states are treated as "open core shell." As the $4f$ localization cannot be properly described within LDA, a self-interaction correction for the $4f$ states is included. In this way, any artificial constraints on the $4f$ charge density employed in earlier first-principles CF calculations are avoided. The calculated CF parameters agree well with recent neutron scattering data.

The calculation of crystal-field (CF) parameters for rare-earth ions in metals from first principles has attracted much attention in recent years,[1–7] since the CF is one of the basic interactions governing the behavior of rare-earth $4f$ electrons in crystals.[8] In particular, the CF is of fundamental importance to the understanding of magnetocrystalline anisotropy in rare-earth metals and compounds.[1] Dilute rare-earth noble metal alloys are ideal model systems to study the origin of crystal fields and to compare results of theoretical investigations with experiment.[9] In such alloys, the interaction between rare-earth ions is negligible because of the dilution, and single-ion behavior can be presupposed. Due to the cubic point symmetry of the rare-earth sites, two parameters are sufficient to describe the CF. No magnetic interaction between the transition metal host and the rare-earth $4f$ states has to be accounted for. Moreover, the electronic structure of noble metals is comparatively simple and well understood. Recently, Hahn, Loewenhaupt, and Frick[9] performed measurements of the CF excitations for Er and Dy impurities in Ag and Au by inelastic neutron scattering. This method is the most direct way of determining CF parameters. Other measuring techniques like Mössbauer spectroscopy, susceptibility, or electron paramagnetic resonance measurements involve a higher amount of ambiguity regarding the determination of CF parameters from experimental data. Thus, the CF parameters obtained in Ref. 9 should be appropriate to test the reliability of theoretical calculations. In particular, the question can be investigated further, whether the CF parameters in the CF model Hamiltonian, Eq. (1) below, do have the same meaning as the electrostatic CF parameters defined in Eq. (2).

The simple point charge model (PCM) of CF cannot explain the experimental values of the CF parameters of rare-earth ions in noble metals.[10] Improved PCM's,[10–15] in particular those taking into consideration the on-site contribution of an electron in a nonmagnetic $5d$ virtual bound state,[10,13,14] yield the correct sign and magnitude of the CF, but fail in predicting differences between the hosts Ag and Au.[9] An *ab initio* calculation of the CF parameters for rare-earth ions diluted in noble metals has, to our knowledge, not been performed up to now. Such a calculation should take into account effects of charge redistribution self-consistently, since the CF is very sensitive to even tiny changes in the charge distribution. Rigid band calculations[16] are based on the assumption that both band structure and electronic charge distribution in the host crystal are not changed if a host atom is substituted by a rare-earth impurity. Therefore, we consider them to be less suitable for describing the CF quantitatively.

The CF Hamiltonian for $4f$ electrons is given by

$$\hat{H}_{\mathrm{cf}} = \sum_{l>0}^{6} \sum_{m=-1}^{l} \Theta_l \hat{O}_l^m \langle r^l \rangle A_l^m \ , \qquad (1)$$

containing the Stevens coefficients Θ_l, the Stevens operator equivalents $\hat{O}_l^m$,[17,18] and expectation values of r^l with the radial $4f$ wave function. Considering the nonspherical part of the Hartree interaction energy of the $4f$ electrons with *all* other charges $\rho(\mathbf{R})$ in the crystal, the formula

$$A_l^m \langle r^l \rangle = \frac{4\pi}{2l+1} \int d\mathbf{R} C_{lm} Y_{lm}(\mathbf{R}) \rho(\mathbf{R}) \int dr \frac{r_<^l}{r_>^{l+1}} r^2 \rho_{4f}(r) \qquad (2)$$

for the CF parameters is obtained,[1,5] with

$$\langle r^l \rangle = \int dr r^{l+2} \rho_{4f}(r) \ , \qquad (3)$$

prefactors C_{lm} and real spherical harmonics Y_{lm} (cf., e.g., Ref. 18), $r_< = \min(r, |\mathbf{R}|)$, and $r_> = \max(r, |\mathbf{R}|)$. For rare-earth sites with cubic point symmetry, Eq. (1) is reduced to[18]

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TABLE I. $4f$ radial expectation values $\langle r^l\rangle$ of Er[$4f^{11}$] and Dy[$4f^9$] in Ag and Au obtained from DF-LDA calculations with self-interaction-corrected $4f$ states (a) in comparison to free R^{3+} ion Dirac-Fock values of Ref. 29(b).

	$\langle r^2\rangle$ (units of a_0^2)	$\langle r^4\rangle$ (units of a_0^4)	$\langle r^6\rangle$ (units of a_0^6)
Er in Ag (a)	0.75	1.56	8.18
Er in Au (a)	0.75	1.58	8.43
Er^{3+} (b)	0.71	1.27	4.82
Dy in Ag (a)	0.82	1.87	10.5
Dy in Au (a)	0.83	1.91	11.1
Dy^{3+} (b)	0.78	1.51	6.05

$$\hat{H}_{\mathrm{cf}} = \Theta_4 A_4 \langle r^4\rangle(\hat{O}_4^0 + 5\hat{O}_4^4) + \Theta_6 A_6 \langle r^6\rangle(\hat{O}_6^0 - 21\hat{O}_6^4) \tag{4}$$

with only two independent CF parameters $A_4 = A_4^0$, $A_6 = A_6^0$. Contributions of the exchange potential to the CF were not taken into consideration.

According to Eq. (2), the parameters A_l^m can be obtained from a calculated charge distribution $\rho(\mathbf{R})$ by real space integration. Our calculations of this charge distribution are based on density-functional theory at the local-density-approximation (LDA) level. The $4f$ states are treated as *open core* states, i.e., the $4f$ shell is considered to remain in its ionic ground state configuration, but is subject to both Hartree and exchange-correlation interaction with the other electrons.[5,19,20] We use a self-consistent optimized linear combination of atomic orbitals (LCAO) method[21] in a scalar relativistic version.[22] The Hartree potential is built up from overlapping spherical site potentials within this method. In this way, nonspherical effects in the "interstitial" region are taken into account self-consistently. In the final step of the self-consistent cycle, the charge density is calculated without any shape restrictions and used to obtain the CF parameters via Eq. (2). The details of the density representation and the evaluation of Eq. (2) follow the lines described in an earlier paper[5] concerning SmCo_5. The dilute rare-earth noble metal alloys were simulated as ordered $M_{31}R$ compounds (M = Ag, Au; R = Er, Dy) composed of fcc-like 32-atom supercells with one noble metal atom in the center substituted by a rare-earth atom. We used the experimental lattice constants of the related pure noble metals, $a = 7.722a_0$ for Ag and $a = 7.708a_0$ for Au.[23] The von Barth–Hedin version[24] for the exchange and correlation potential was employed.

$4f$ states of heavy rare-earth atoms in intermetallics are known to be strongly localized due to Coulomb correlation. This localization cannot be described by density-functional (DF) calculations entirely within LDA but is accounted for by the above-mentioned $4f$ core state treatment. However, the LDA binding energy of the open core $4f$ states is much too small and sometimes even negative if the experimental $4f$ configuration is fixed. That means, $\langle r^l\rangle$ would be appreciably overestimated or $\langle r^l\rangle \to \infty$, respectively. In previous first-principles CF calculations strictly localized $4f$ states were modeled by rather artificial methods.[1–7] Either the $4f$ charge was restricted to the atomic sphere by adding a rectangular potential well and cutting off the r integration in Eq. (2) at a certain radius,[4,6,7,25] the $4f$ states were compressed by introducing an attractive r^4 potential,[5] or the r integration in Eq. (2) was cut off at the atomic sphere radius, where the logarithmic derivative of the radial $4f$ wave function was attached self-consistently to a Hankel function.[3,26] All these methods are arbitrary to some extent, since they involve at least one adjustable parameter determining the large-r asymptotic behavior of the $4f$ radial wave function and the calculated CF parameters should depend sensitively on this tuning procedure. To circumvent this problem we propose another way of mod-

TABLE II. Calculated CF parameters for Er[$4f^{11}$] and Dy[$4f^9$] in Ag and Au obtained from DF-LDA calculations with self-interaction-corrected $4f$ states, decomposed into on-site, nearest neighbor (NN) shell, and remaining lattice contributions, in comparison with experimental data from Ref. 9.

$A_4\langle r^4\rangle$ (K)	Er in Ag	Dy in Ag	Er in Au	Dy in Au
On site	−24.2	−27.2	−35.1	−38.4
NN shell	17.4	20.4	19.6	26.1
Lattice	0.0	0.0	−0.5	−0.6
Total	−6.8	−6.8	−16.0	−12.9
Experiment[a]	−12.1±1.1	−15.3±2.1	−18.5±1.2	−30.0±1.9
$A_6\langle r^6\rangle$ (K)	Er in Ag	Dy in Ag	Er in Au	Dy in Au
On site	−0.7	−0.8	−0.9	−1.1
NN shell	7.5	9.1	9.8	13.5
Total	6.8	8.3	8.9	12.4
Experiment[a]	6.4±0.2	6.5±0.2	4.9±0.2	1.3±0.2

[a] Reference 9.

eling the $4f$ localization in the CF calculations, namely by applying a self-interaction correction (SIC) to the $4f$ states. Self-interaction corrections to the local-density approximation eliminate the unphysical interaction of an electron with itself which is not completely canceled in the LDA and, thus, improve LDA calculations for localized systems.[27] In particular, SIC-LDA calculations yield the correct large-r asymptotic behavior of the effective one-particle potential and provide substantial corrections to the energy eigenvalues of localized states. For example, such calculations were recently found to account for the spectroscopic splitting of the f band in Pr metal.[28] Including SIC's in the calculation of the $4f$ radial density results in a decrease of the energies of the occupied $4f$ states by about 1.0 Rys and a stronger localization of the $4f$ charge density. The Coulomb and exchange-correlation parts of the SIC potential were calculated from the spherically averaged orbital densities in each iteration step of the self-consistent cycle.

The $4f$ radial expectation values $\langle r^l \rangle$ we obtained for Er and Dy impurities in Ag and Au are compared with the related values for free Er^{3+} and Dy^{3+} ions from a Dirac-Fock calculation[29] in Table I. The latter have been used by experimentalists[9] to deduce the "bare" CF parameters A_l^m from the quantities $A_l^m \langle r^l \rangle$, which are directly connected to experimental data. However, the $\langle r^l \rangle$ values in the crystal can be expected to be enhanced in comparison with the free-ion values, as is confirmed by the data exhibited in Table I. For this reason, the comparison between theory and experiment should be done with respect to the product $A_l^m \langle r^l \rangle$. Our results for the CF parameters for Er and Dy impurities in Ag and Au are summarized in Table II. The main contributions to $A_l^m \langle r^l \rangle$ originate from on-site and nearest neighbor shell site densities. Lattice contributions arising from the next nearest and higher neighbor shells turn out to be negligible. In the case of $A_4 \langle r^4 \rangle$, the dominating on-site contribution is negative and changes the sign of this CF parameter. The main part of this contribution can be identified with that of the proposed[10] $5d$ virtual bound state. It is proportional to the difference in the $5d$ partial occupation numbers $n_{e_g}/2 - n_{t_{2g}}/3$, which is found to be about -0.02 in Ag and about -0.03 in Au. Mulliken population analysis yields a net valence electron population on the rare earth site of 1.1–1.2 of predominantly d character. Sign and magnitude of all calculated CF parameters agree with the related experimental data of Ref. 9. The relation of fourth-order CF parameters for Er in Ag and Au is reproduced correctly, while this relation is reversed for the sixth-order parameters compared to the experimental situation (Fig. 1). Our results for Dy in Ag and Au are similar. The differences in the fourth-order parameters in the hosts Ag and Au are primarily due to changes of the on-site contributions. The large difference between the experimental values of the sixth-order parameter for Dy and Er in Au is hard to understand and cannot be obtained in our calculations, assuming the rare-earth ions to be very similar with respect to the shape of their radial $4f$ density and, thus, yielding only small alterations of the CF parameters between different impurities in the same host. Another point to be discussed when comparing our results to experiment is that the rare-earth concentration of typically 0.08 and 1 at. % in the measurements[9] is lower than about 3 at. % in the calculations. However, enlarging the supercell would not change the results of our CF calculations significantly, since site charges in second and higher neighbor shells of a rare-earth ion do only marginally contribute to the CF (cf. Table II). Finally, a complete full potential treatment requires one to include intra-atomic nonsphericity effects self-consistently in the calculation of the charge distribution.

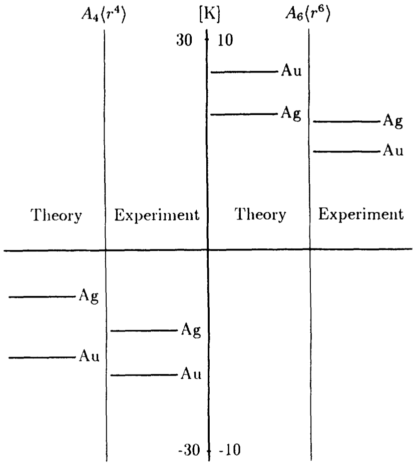

FIG. 1. Comparison between theoretical (present calculation) and experimental (Ref. 9) CF parameters of Er in Ag and Au.

In conclusion, we have shown that the crystal-field parameters for rare-earth impurities in noble metals can be calculated from first principles in the framework of the crystal-field model (1). Our results are in good agreement with recent data from neutron scattering measurements, except those for Dy in Au. Artificial constraints on the $4f$ radial charge density can be avoided if the self-interaction correction for the localized $4f$ states is taken into account.

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