

## Exchange Corrections to the Crystalline Field Parameter $C_4$ for Rare Earths in the Noble Metals\*

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A suggestion of Coles and Orbach involving the formation of virtual bound states is shown to account for the fourth-order crystalline field parameter in simple rare-earth-doped metals.

In a recent paper,<sup>1</sup> Williams and Hirst reported measurement of magnetic susceptibilities of dilute alloys of heavy rare earths in Ag and Au, and attributed departure of the susceptibility from a Curie-Weiss behavior to the effect of crystal fields. Williams and Hirst found that their results could be fitted using conventional crystal field theory, with the appropriate symmetry, provided  $C_4$  was negative. The magnitude, as well as the sign, differs from that calculated using a point-charge model. Invoking the hypothesis of a cubic crystal field split by a  $5d$  nonmagnetic virtual bound state (vbs) at the rare-earth site, as proposed by Coles and Orbach, a large negative contribution to  $C_4$  was obtained. The magnitude, however, appeared to be an order of magnitude larger than required by the crystal-field-theory fit, and it was necessary to invoke some mechanisms which would reduce this contribution. Specifically, they proposed two mechanisms: "First, because the finite width of the vbs will cause some population of the  $5d\gamma$ -type orbitals, with consequent cancellation of the nonspherical part of the potential; and second, because the total  $5d$  population will decrease from one towards zero as the  $5d$  energy rises from below to above the conduction-electron Fermi energy."<sup>1</sup> Their calculation utilized only the Coulomb interaction between the  $4f$  and  $5d$  electrons. The exchange term was omitted "because of the small  $4f$ - $5d$  overlap." The purpose of this note is to point out that the exchange contribution to  $C_4$  which they omitted is not small, cancels a large fraction of the Coulomb term, so that the mechanisms they proposed do not appear to be the dominant ones.

As noted in Williams and Hirst's treatment, the three  $5d\epsilon$  orbitals have lower energy than the  $5d\gamma$

orbitals in a cubic host. The vbs model correspondingly requires that it is three (nonmagnetic)  $5d\epsilon$  orbitals which contribute to the effective crystalline field experienced by the (magnetic)  $4f$  electrons. Let the state of a  $4f$  electron be labeled by  $|l^a m^a\rangle$  and the three  $5d\epsilon$  orbitals be denoted by  $\sum_i \alpha_i |l^{b_i} m^{b_i}\rangle$ ,  $\sum_i \beta_i |l^{b_i} m^{b_i}\rangle$ ,  $\sum_i \gamma_i |l^{b_i} m^{b_i}\rangle$ , the latter being linear combinations of atomic orbitals with constant coefficients  $\alpha$ ,  $\beta$ , and  $\gamma$ . The Coulombic interaction  $E_{\text{Coul}}$  between a  $4f$  state and the first  $5d\epsilon$  orbital is given by<sup>2</sup>

$$E_{\text{Coul}} = \sum_i \alpha_i^2 \langle l^a m^a | \langle l^{b_i} m^{b_i} | \frac{e^2}{r_{12}} | l^a m^a \rangle | l^{b_i} m^{b_i} \rangle$$

$$= \sum_i \alpha_i^2 \left( \sum_k a^k (l^a m^a, l^{b_i} m^{b_i}) F^k(n^a l^a, n^{b_i} l^{b_i}) - \delta(m_s^a, m_s^{b_i}) \sum_k b^k (l^a m^a, l^{b_i} m^{b_i}) G^k(n^a l^a, n^{b_i} l^{b_i}) \right),$$

where  $a^k$  and  $b^k$  are coefficients obtained from angular integrations and tabulated by Condon and Shortely.  $F^k$  and  $G^k$  are radial Coulomb and exchange interelectronic integrals defined by

$$F^k(n^a l^a, n^b l^b) = e^2 \int_0^\infty \int_0^\infty \frac{r_1^k}{r_2^{k+1}} \times R_1^2(n^a l^a) R_2^2(n^b l^b) dr_1 dr_2,$$

$$G^k(n^a l^a, n^b l^b) = 2e^2 \int_0^\infty dr_2 \int_0^{r_2} \frac{r_1^k}{r_2^{k+1}} R_1(n^a l^a) R_2(n^b l^b) \times R_2(n^a l^a) R_2(n^b l^b) dr_1.$$

The summation is carried out for each of the three  $5d\epsilon$  orbitals and the average of the results is taken, in recognition of the fact that each orbital is

TABLE I. Comparison of various contributions to  $C_4$ .

Rare earth	$C_4$ ( $^\circ\text{K}$ )		Ratio (exchange/direct)	$C_4$ ( $^\circ\text{K}$ )		
	from direct Coulomb	$C_4$ ( $^\circ\text{K}$ ) from exchange		Coulomb and exchange	$C_4^{\text{expt}}$ ( $^\circ\text{K}$ ) in Ag	$C_4^{\text{expt}}$ ( $^\circ\text{K}$ ) in Au
Dy <sup>3+</sup>	-226.07	192.73	85%	-33.34	-70	...
Er <sup>3+</sup>	-226.89	195.20	86%	-31.69	-70 ± 2	-32 ± 4
Yb <sup>3+</sup>	-220.38	189.04	86%	-31.34	...	-27 ± 3

equally likely to form a bound state. It is important as a next step that the interaction-energy matrix be evaluated in full, and made traceless, in order to be cast in the usual crystal field form. Upon completion of this prescription one finds, for the case  $m^a = 0$ , as an example,

$$E_{\text{Coul}} = -\frac{14}{693} F^4(4f, 5d) + \frac{1}{70} G^1(4f, 5d) + \frac{2}{315} G^3(4f, 5d)$$

$$+ \frac{1}{3049.2} G^5(4f, 5d).$$

The crystal field parameter  $C_4$  may now be obtained by dividing the above quantity by the appropriate operator equivalent matrix element and multiplying factor.<sup>3</sup>

Using the Coulomb and exchange integrals<sup>4</sup> from Hartree-Fock calculations

for Dy <sup>3+</sup> :	$F^4(4f, 5d) = 11710.2 \text{ cm}^{-1}$ ,	$G^1(4f, 5d) = 10185.2 \text{ cm}^{-1}$ ,
	$G^3(4f, 5d) = 8510.6 \text{ cm}^{-1}$ ,	$G^5(4f, 5d) = 6541.2 \text{ cm}^{-1}$ ;
for Er <sup>3+</sup> :	$F^4(4f, 5d) = 11752.4 \text{ cm}^{-1}$ ,	$G^1(4f, 5d) = 10331.0 \text{ cm}^{-1}$ ,
	$G^3(4f, 5d) = 8585.6 \text{ cm}^{-1}$ ,	$G^5(4f, 5d) = 6584.6 \text{ cm}^{-1}$ ;
for Yb <sup>3+</sup> :	$F^4(4f, 5d) = 11415.5 \text{ cm}^{-1}$ ,	$G^1(4f, 5d) = 10010.8 \text{ cm}^{-1}$ ,
	$G^3(4f, 5d) = 8304.6 \text{ cm}^{-1}$ ,	$G^5(4f, 5d) = 6362.4 \text{ cm}^{-1}$ ,

one finds the results displayed in Table I.

As can be seen from Table I, the exchange contribution is opposite in sign to the Coulomb, and (roughly) 85% of it in magnitude. The net contribution of the  $5d$  vbs to  $C_4$  is thus the correct magnitude to account for the experimental crystal field parameters used by Williams and Hirst to fit their data. The bare-point-charge contribution is about

five times smaller and of opposite sign, so that the Coles-Orbach suggestion may in fact satisfactorily account for the fourth-order crystalline field parameter in simple rare-earth-doped metals.

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<sup>1</sup>G. Williams and L. L. Hirst, *Phys. Rev.* **185**, 407 (1969).

<sup>2</sup>E. V. Condon and G. H. Shortley, *The Theory of Atomic*

*Spectra* (Cambridge U. P., New York, 1953), Chap. IV.

<sup>3</sup>K. W. H. Stevens, *Proc. R. Soc. A* **265**, 209 (1952).

<sup>4</sup>We are grateful to Professor A. J. Freeman and to Dr. J. V. Mallow for providing us with these values prior to publication (private communication).