

CRYSTALLINE ELECTRIC FIELD EFFECTS IN DILUTE ALLOYS OF RARE EARTH METALS

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A theory is developed for interpreting the effects of the crystalline electric field in non-magnetic metals containing small quantities of magnetic rare earth impurities. The experimentally detected regularities in the behaviour of the crystalline-electric-field-Hamiltonian parameters for various dilute alloys with heavy rare earth metals have been analyzed. Parameters of the model crystal potentials are determined for the non-magnetic metals magnesium, scandium, yttrium and lutetium. It can be concluded that the Friedel oscillations in the effective electrostatic interaction between the ions in the metals have observable consequences for the crystal-field parameters.

1. Introduction

Dilute alloys of rare earth metals (REM) with non-magnetic metals are convenient subjects for studying the effects of the crystalline electric field (CEF). The advantage of these systems is that the non-magnetic nature of the matrix metal excludes magnetostrictive effects, and the large distances between the rare earth ions weaken the exchange interaction. Among the non-magnetic metals, lutetium and yttrium are closest to the magnetic REM in their structure and properties. Though scandium and magnesium under normal conditions differ noticeably from the REM in their parameters, they have a hexagonal close-packed lattice like most of the REM. The CEF effects in dilute alloys of REM with the four above-mentioned non-magnetic metals have been investigated experimentally in detail [1–9]. The manifestations of the CEF effects were studied both in the magnetic properties [1–4] and in the inelastic magnetic scattering of cold neutrons [5–8]. As

mentioned by Touborg [9], the experimentally obtained results are not in accordance, not even qualitatively, with the simplest CEF model of effective point charges (MEPC) [10]. A number of systematic regularities in the behaviour of the CEF Hamiltonian coefficients can be extracted from the results of the experimental papers [1–9]. Among these regularities one conventionally distinguishes two “strong” peculiarities: (1) a greater value of the sixth-order CEF parameters, as compared with that calculated in the MEPC, which are relatively insensitive to the matrix type, and (2) a strong correlation between the second-order CEF coefficients and the lattice parameters of the various matrices. The other peculiarities are relatively weaker: (3) a positive sign of the B_{40}/β_j ratio (unlike the negative sign of this ratio in the MEPC), and (4) a weak but still noticeable irregular variation of the CEF parameters for various rare earth (RE) ions dissolved in one and the same matrix.

In the following it will be shown that the

“strong” peculiarities are related to an oscillating spatial variation of the crystalline field potential whereas the “weak” ones, apparently, are introduced because of the reaction of the outer and inner (with respect to the 4f-electrons) electronic shells of the RE ions to the crystalline field of the metal (the so-called “shielding” of the crystalline field).

2. Interpretation of CEF effects in dilute alloys of heavy REM

The CEF Hamiltonian for hexagonal symmetry can be written in the following form:

$$H_{\text{CEF}}^{\text{hex}} = B_{20}O_{20} + B_{40}O_{40} + B_{60}O_{60} + B_{66}O_{66}, \quad (1)$$

O_{nm} are the Stevens equivalent operators [10] and B_{nm} ($n = 2, 4, 6$; $m = 0, 6$) are written as follows:

$$B_{nm} = eb_n \sum_{\nu=0}^{\infty} A_{nm}^{\nu} \langle r^{n+2\nu} \rangle (1 - \sigma_{n,\nu}), \quad (2)$$

where e is the electron charge, and b_n are the Stevens factors usually denoted as $\alpha_J = b_2$, $\beta_J = b_4$ and $\gamma_J = b_6$ which have been calculated for the ground state of all the three-fold positively charged RE ions [10]. $\langle r^n \rangle$ are the average values of the n th power of the f-electron radius [11–13]. A_{nm}^{ν} are the lattice sums containing various combinations of derivatives of the metal crystal potential (CP) $V(\mathbf{r})$ [14,15]. $A_{nm}^{\nu=0}$ have to be interpreted as being due to the contribution of external charges to the CP $V(\mathbf{r})$ which satisfies the Laplace equation $\nabla^2 V = 0$, whereas A_{nm}^{ν} ($\nu = 1, 2, \dots$) are due to the non-spherical part of the charge distribution of the conduction electrons near the 4f-shell. Assuming a general central-force CP:

$$V(\mathbf{r}) = \sum_i V_i(|\mathbf{R}_i - \mathbf{r}|), \quad (3)$$

the lattice sums A_{nm}^0 ($n = 2, 4, 6$; $m = 0, 6$) in the hexagonal case are those given in ref. [16] (the model used in this paper is equivalent in many respects with that of ref. [15]). $\sigma_{n,0}$ are the so-called “shielding factors” of the external-charge part of the CP $V(\mathbf{r})$ [17,18]. The rest $\sigma_{n,\nu}$ ($\nu = 1, 2, \dots$) are the “shielding factors” of the field due to the local charge density, which are very uncertain, and in

subsequent calculations we simply neglect these terms, assuming $\sigma_{n,\nu} = 1$ for $\nu = 1, 2, \dots$

In order to perform a qualitative analysis of the above-mentioned regularities shown by the CEF Hamiltonian coefficients we use two types of model potentials V_i . These potentials describe the main features of the CEF space distribution in a metal, with a minimum number of parameters to be varied.

$$V_i(r) = \frac{Ze}{r} \exp(-\beta r) \cos(\alpha r + \gamma) \quad (4)$$

and

$$V_i(r) = \frac{A}{(k_f r)^3} \cos(\alpha r + \gamma), \quad (5)$$

where k_f is the electron wave vector on the Fermi surface approximated by the formula $k_f = (3\pi^2 Z/v_A)^{1/3}$, Z is the ion valence, and v_A is the volume per ion. The potential V_i (4) can be easily transformed into a pure Coulomb potential, $V_{\text{Coul}} = Ze/r$, or into one of the Yukawa type $V_{\text{Yu}} = (Ze/r) \exp(-\beta r)$ by a proper choice of the parameters. The potential V_i (5) is a well-known asymptotic form of the two-particle interaction potential [19]. Though one obtains convergent expressions for the CEF Hamiltonian coefficients when using V_i (5), the slow decrease of $V_i \propto 1/r^3$ makes it necessary to perform the summation over a great number of coordination spheres of ions.

The lattice parameters of the matrix metals, which are used in the calculations, are presented in table 1. The average values of the n th powers of the 4f-electron radius for the RE ions [13] are given in table 2. In order to reduce the number of variable parameters, the shielding factors are assumed to be the same for all the heavy RE ions,

Table 1
Parameters of the matrix metal lattices

	Mg	Sc	Lu	Y
a (Å)	3.1930	3.3088	3.5052	3.6482
c (Å)	5.1854	5.2680	5.5494	5.7318
v_A (Å ³)	22.89	24.97	29.52	33.03
$\delta = (8/3)^{1/2} - c/a$	0.009	0.041	0.050	0.062

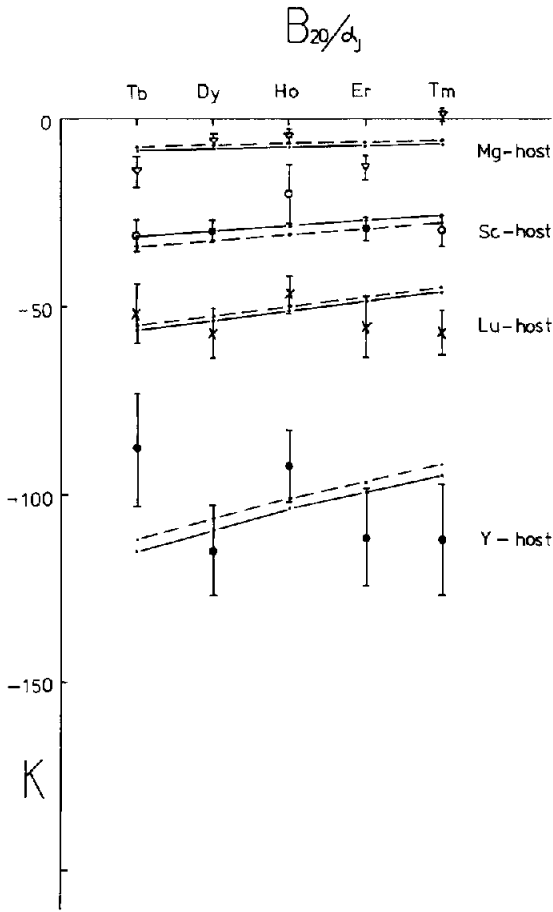


Fig. 1. The 2nd-order coefficients B_{20}/α_J for dilute alloys of heavy REM with Mg, Sc, Lu and Y. The experimental data [4,8,9]: ∇ - Mg, \circ - Sc, \times - Lu, and \bullet - Y. The vertical lines denote the uncertainties in B_{20}/α_J . The theoretical results are given by dots and connected for convenience: (a) the dashed line indicates the use of the V_i -potential (4) with the parameters from table 4; (b) the solid line shows the results obtained using the V_i -potential (5) with the parameters taken from table 5.

and two of these are considered to be fixed, namely $\sigma_{2,0} = 0.8$ and $\sigma_{6,0} = 0$. These values are close to those calculated for Pr^{3+} and Tm^{3+} [18], which are, unfortunately, the only results available in the literature. The $\sigma_{4,0}$ factor is used as a fitting parameter like the three parameters which determine either one of the potentials V_i (4) or (5). Figs. 1-3 show the comparison achieved between the experimental [4,8,9] and the theoretical values of the ratios B_{20}/α_J , B_{40}/β_J and B_{60}/γ_J for the

Table 2
Average values of $\langle r^n \rangle$ for heavy RE ions [13]

	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}
$\langle r^2 \rangle$ (au)	0.900	0.854	0.812	0.774	0.740
$\langle r^4 \rangle$ (au)	2.167	1.971	1.802	1.655	1.528
$\langle r^6 \rangle$ (au)	11.480	10.120	8.991	8.040	7.242

heavy RE ions dissolved in Mg, Sc, Lu and Y. The experimental [4,8,9] and calculated values of the sixth-order coefficient ratio B_{66}/B_{60} are presented in table 3. The parameter values of the potentials V_i (4) and (5) and the factor $\sigma_{4,0}$ which are used in these calculations are presented in tables 4 and 5.

We begin the analysis of the peculiarities in the

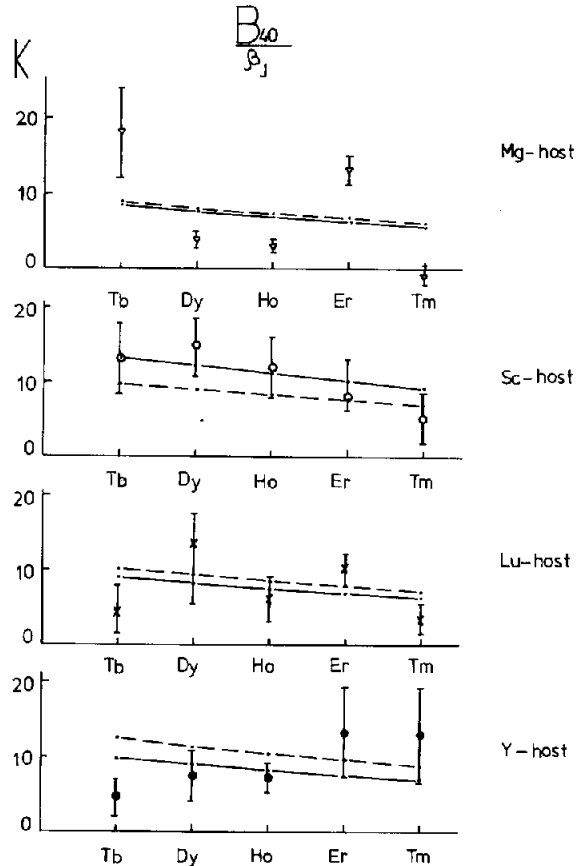


Fig. 2. The 4th-order coefficients B_{40}/β_J for dilute alloys of heavy REM with Mg, Sc, Lu and Y. The symbols are the same as those in fig. 1.

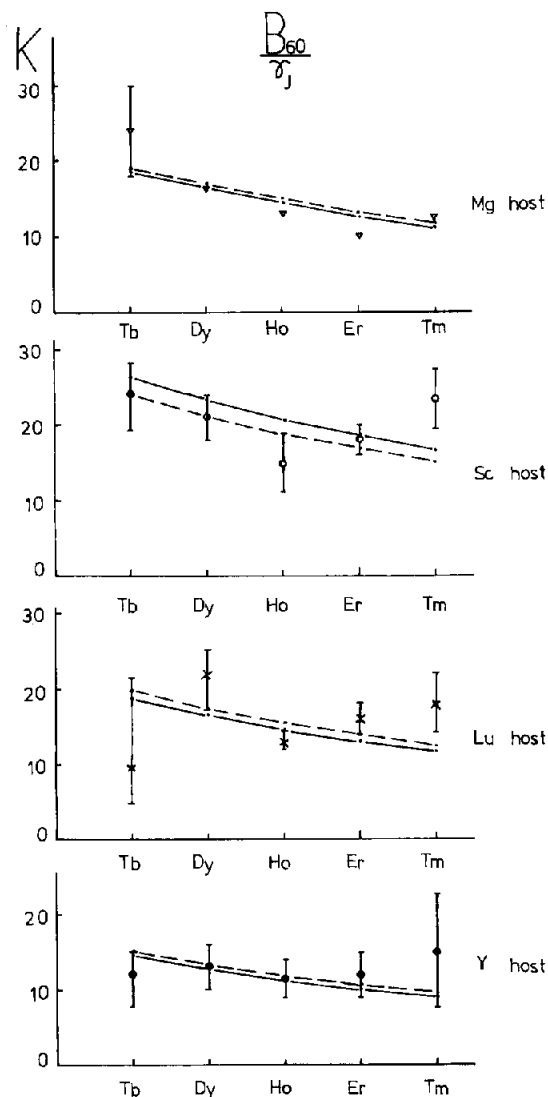


Fig. 3. The 6th-order coefficients B_{60}/γ_J for dilute alloys of heavy REM with Mg, Sc, Lu and Y. The symbols are the same as those in fig. 1.

Table 3
Experimental [4,8,9] and calculated ratios of the 6th-order coefficients B_{66}/B_{60}

	Tb	Dy	Ho	Er	Tm	Theory $V_i(4)$	Theory $V_i(5)$
Mg	77/8	8.5	9.2	11.1	8.6	9.5	10.0
Sc	-	9.6	8.5	10.2	-	9.1	9.2
Lu	-	9.0	9.6	10.4	-	9.1	9.0
Y	-	8.2	10.3	11.1	-	9.6	9.5

Table 4
Values of parameters of the V_i -potentials (4) and $\sigma_{4,0}$ used to calculate the CEF Hamiltonian coefficients given in figs. 1-3 and presented in table 3

	Z	β (\AA^{-1})	α (\AA^{-1})	γ	$\sigma_{4,0}$
Mg	+2	1.44	2.830	-4.64	1.3
Sc	+3	1.27	2.523	-3.96	1.3
Lu	+3	1.10	2.407	-4.00	1.3
Y	+3	1.02	2.474	-4.65	1.3

Table 5
Values of parameters of the V_i -potentials (5) and $\sigma_{4,0}$ used to calculate the CEF Hamiltonian coefficients given in figs. 1-3 and presented in table 3

	Z	A (volt)	α (\AA^{-1})	γ	$\sigma_{4,0}$
Mg	+2	43.2	2.298	-2.51	1.1
Sc	+3	93.6	2.346	-2.96	1.1
Lu	+3	93.6	2.212	-2.85	1.1
Y	+3	93.6	2.495	-4.67	1.1

behaviour of the CEF Hamiltonian coefficients, mentioned in the introduction, with the "strong" ones. The Lu-Ho system is taken as an example, and the theoretical values of the sixth-order coefficients obtained from the potential $V_i(4)$, with the parameters of table 4, are compared in table 6 with the results derived from the Yukawa and the Coulomb potential. The differences in the coefficients B_{60} and B_{66} for the three types of potentials arise mainly from the nonmonotonic or oscillating nature of the first potential ($\alpha \neq 0$) which results in considerably greater values of its higher derivatives as compared with those of V_{iYU} and V_{iCoul} .

The second-rank coefficients B_{20}/α_J correlate

Table 6
The CEF Hamiltonian 6th-order coefficients of the Lu-Ho system for various model potentials

	$V_i(4)$ $\alpha = 2.407$ $\gamma = -4.00$ $\beta = 1.10$	$V_{iYU}(4)$ $\alpha = 0$ $\gamma = 0$ $\beta = 1.10$	$V_{iCoul}(4)$ $\alpha = 0$ $\gamma = 0$ $\beta = 0$
B_{60}/γ_J (K)	15.5	2.3	4.2
B_{66}/γ_J (K)	141	20	38

both with the atomic volume v_A of the matrix metal and with $\delta = (8/3)^{1/2} - c/a$, i.e. the deviation of the c/a -ratio from its ideal value. The dependence on δ follows from the vanishing of B_{20}/α_J by symmetry if $\delta = 0$, implying B_{20}/α_J to be proportional to δ to leading order. Accepting this dependence, it is found that the experimental results shown in fig. 1 are very well described by the following expression

$$B_{20}/\alpha_J = C_{(\text{RE})} Z v_A^3 \delta \quad (6)$$

with $C_{(\text{RE})} = -0.015 \text{ K}/\text{\AA}^9$ for the average heavy RE-element. Both v_A and δ increase steadily through the sequence Mg, Sc, Lu and Y (see table 1). The simple Coulomb potential predicts $B_{20}/\alpha_J \propto Z v_A^{-1} \delta$, and is therefore unable to account for the observed variation with v_A . In contrast, the CP (5) with the parameters given in table 5, for instance, accounts well for the experimental B_{20}/α_J . The strength of the potentials considered, $A/(k_f r)^3$, measured relative to the Coulomb potential at the first coordination sphere, is about the same (≈ 0.06) in all the four metals. This means that the strong increase in the magnitude of B_{20}/α_J with v_A originates from the oscillatory modulation of the CP (5) alone. Much the same can be said about the other CP (4).

Let us proceed to the "weaker" peculiarities in the behaviour of the CEF Hamiltonian coefficients, mentioned in the Introduction. The positive magnitude of the ratio B_{40}/β_J in the model calculations was obtained only when choosing the "shielding factor" $\sigma_{4,0}$ to be greater than one (see tables 4 and 5). This is inconsistent with the calculated value $\sigma_{4,0} = 0.045$ for Tm^{3+} [18]. At present we are not able to explain this disagreement. It might be necessary to take into account the direct Coulomb and exchange interactions between the electrons of the RE ions and the conduction electrons, when calculating the shielding factors $\sigma_{n,\nu}$, instead of regarding the RE ion as "free". It might also indicate that our implicit assumption that the phase $(\alpha r + \gamma)$ in the potentials (4) or (5) has to be near to $3\pi/2$ at the first coordination sphere (see also ref. [13]), is not adequate.

The magnitude of the coefficients B_{nm} (2) of

the CEF Hamiltonian is determined by both the CP space distribution (by means of the lattice sums A_{nm}^v) and the product of the two constants $\langle r^n \rangle$ and $(1 - \sigma_{n,\nu})$, which depend on the properties of the RE ion. Because of the assumption that the shielding factors $\sigma_{n,\nu}$ are constants, the calculated coefficients B_{n0}/b_n ($n = 2, 4, 6$) presented in figs. 1–3 reflect the change of $\langle r^n \rangle$ for the heavy REM – a gradual decrease with the increase of the atomic number of the ion (see table 2). There are systematic deviations of some significance from the simple $\langle r^n \rangle$ -scaling behaviour correlating mainly with the REM considered, which indicates a variation of $\sigma_{n,\nu}$ through the series of heavy REM. However, some of the results, especially those obtained in the magnesium-alloys, indicate a more complex interplay between the 4f- and the conduction electrons than we have been considering in this analysis. The aim of the present paper is a qualitative analysis of the CEF Hamiltonian of RE ions placed in non-magnetic metallic surroundings, and one should treat the CP parameters given in tables 4 or 5 only as heuristic values satisfactorily describing the general regularities.

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