II. EXPERIMENTAL RESULTS

CRYSTALLINE FIELD EFFECTS IN METALS

BY

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I. INTRODUCTION

This work discusses crystalline field effects in metals (dilute alloys and inter-metallic compounds) with emphasis on Electron Paramagnetic Resonance (*EPR*) experiments.

Electron Spin Resonance of localized moments yield two kinds of information concerning the crystalline field:

(a) The g value (isotropic or unisotropic) exhibit information about the ground state crystalline field splitting.

(b) The *EPR* thermal broadening might give some knowledge about the relative position of the first excited crystalline field level or even the overall splitting. This is because of the close proximity of the excited state which causes departure from linearity of the linewidth versus temperature expected for isolated ground state. This deviation is due to off diagonal matrix elements of the localized-conduction electrons exchange coupling between the ground state and excited states. Such behavior in the *EPR* thermal broadening has been demonstrated previously by Davidov *et al.* [1] and Rettori *et al.* [2] for the systems *Au:Er*, *Rh:Er* and *Ir:Er*.

Part (b) of this work was represented in the Conference by K. Baberschke. There-fore, in the present paper we shall omit (b) and discuss some new aspects of (a).

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The observation of crystalline field effects in metals is related to the general problem of localized moments in metals.

Traditionally, there are two approaches to the solution of this problem: (a) the Friedel-Anderson approach [3, 4] and (b) the Kondo approach or the ionic model [5]. Both these approaches in their original form neglect the Coulomb interaction between local electrons responsible for the ionic configuration and emphasize more the itinerant aspect of the problem. Recently, Hirst [6] extended the ionic model to include Hund's rule correlations. It seems that this model is more successful in the interpretation of the "insulator-like" phenomena as hyperfine spectra, fine-structure and in general the sharp *EPR* resonances observed.

We shall adopt the ionic model and use crystalline field Hamiltonian initially developed for the case of rare-earth ions in insulators, as given by Lea, Leask and Wolf (LLW) [7]. In the notation of LLW, $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ are the fourth order and sixth order crystalline field parameter respectively; x is proportional to their ratio.

The *EPR* work was performed on rare earth in dilute alloys and intermetallic compounds. In the case of dilute alloys we always found $A_4 \langle r^4 \rangle$ to be negative and $A_6 \langle r^6 \rangle$ positive (with the exception of *Pd:Er* and *Pd:Dy* where both these parameters are negative). This is in disagreement with the point charge model expected for *fcc* structure with positive charges on the ligands. In the case of inter-metallic compounds the sign of the fourth order parameter agrees with the point charge model. A possible interpretation for this difference is suggested.

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Under cubic crystalline field the multiplet J, associated with the rare earth ion, is split into quartets (Γ_8) and doublets (Γ_7 and Γ_6). The multiplicity of these levels depends on J.

If the crystalline field splitting ground state is Γ_8, the *EPR* spectra is usually anisotropic. In this case, as was demonstrated previously [8], the value of x (or the ratio $A_4 \langle r^4 \rangle / A_6 \langle r^6 \rangle$) can be determined. This information together with the tabulated data of LLW yield the sign of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$. If, however, the ground state is doublet (Γ_7 or Γ_6) additional information is needed for determination of the sign of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$. This information is provided by further data using other experimental techniques or sometimes by *EPR* observation of two ions in the same host. In the latter case, we assume that the crystalline field does not change appreciably across the 4*f* series and at least retains its sign and magnitude. This assumption, as well as LLW tabulated data, is sometimes enough for the prediction of the sign of the crystalline field parameters.

Table I exhibits the available experimental data on dilute alloys and intermetallic compounds having cubic structure.

III. DISCUSSION

We would like now to analyze the experimental data described above. Unfortunately, quantitative calculations are impossible at this stage and we shall restrict ourselves, therefore, to a discussion on the sign of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ only.

For *fcc* structure (12 coordination number), the point charge model predicts positive values for both crystalline-field parameters. The experimental results for dilute alloys, however, indicate negative $A_4 \langle r^4 \rangle$. A virtual bound state (*VBS*) model was suggested [19] to explain this "discrepancy". The arguments in favor of this model are as follows: Because of the difference in valence between the tri-valent rare-earth and that of the host, there will be screening charge around the rare-earth ion to satisfy the Friedel rule. The screening electrons must be in states orthogonal to the rare-earth core. It can be shown that the low lying state which satisfies this requirement is the $5d$ state. This $5d$ electron is nonmagnetic and in metal can be considered as a virtual bound state. The positive charge on the ligands (in the case of cubic noble metals) can split this $5d$ *VBS* into three, so-called, $d\varepsilon$ orbitals (xy, yz, zx) and two $d\gamma$ orbitals ($x^2 - y^2$, z^2). This crystalline field splitting produces an aspherical charge distribution which can affect the crystalline field experienced by the $4f$ electrons. Aspherical charge distribution associated with the $5d$ *VBS* is possible if the width of the *VBS* is smaller than the crystalline field splitting of the *VBS*.

The overall charge distribution associated with the $d\varepsilon$ orbitals has a *fcc*-like symmetry; that associated with the $d\gamma$ has octahedral symmetry. Thus, for *fcc* metals with positive charges on the ligands, we expect $d\varepsilon$ orbitals to lie lowest and their contribution to $A_4 \langle r^4 \rangle$ will be the same as expected from *fcc*-like symmetry with negative charge distribution i.e. negative $A_4 \langle r^4 \rangle$. If, however, the charge on the ligands is negative, the $d\gamma$ will lie lowest. Then the contribution to $A_4 \langle r^4 \rangle$ for the *VBS* will be positive as expected from octahedral-like charge distribution with negative charges (electrons) on the ligands. In a similar way, one can analyze the contribution of the *VBS* to $A_4 \langle r^4 \rangle$ in the other cubic hosts (*NaCl* and *CsCl* structures with different charges on the ligands). Table II exhibits the values of $A_4 \langle r^4 \rangle$ for the *VBS* model. For comparison the crystalline field parameters expected according the point charge (*PC*) model are also given. It is clearly seen that the contribution of the *VBS* to $A_4 \langle r^4 \rangle$ is always opposite in sign to that of the *PC* model. Symmetry considerations indicate that $5d$ *VBS* *cannot* contribute to $A_6 \langle r^6 \rangle$. As demonstrated by Dixon and Dupree [20], the f-like component in the conduction electron's wave function can contribute to $A_6 \langle r^6 \rangle$; its contribution to $A_4 \langle r^4 \rangle$ is much less than that of the $5d$ *VBS* and we shall neglect it. In Table II, we also give the f-like contribution to $A_6 \langle r^6 \rangle$. This is also an "anti-shielding" mechanism and we expect its contribution to $A_6 \langle r^6 \rangle$ to be opposite in sign to that of the point charge model.

Let us now consider the crystalline field parameters in intermetallic compounds. Comparison of the experimental results (Table I) with the prediction of the three models (*PC, VBS* and *f*-like contribution, Table II) for the various structures, indicates that the *PC* model dominates here. In metals, where conduction electrons might play a role, the success of such a naive model is very surprising. It should be stressed, however, that intuitively one expects much larger contribution of the *VBS* to $A_4 \langle r^4 \rangle$ in dilute alloys than in intermetallic compounds. This is mainly due to the much smaller screening effect of the rare-earth ions in the latter. For the case of intermetallic compounds with *NaCl* structure (*LaSb, LaBi* . . .) the charges on the *Sb* or *Bi* are between -2 and -3 (and probably close to -3 depending on their location in the periodic table). Because of the large electro-negativity of these ions, the screening of the rare-earth ions is small here. A similar tendency is found in intermetallic compounds of Cu_3Au structure.

In summary, the main issue of this work is to point out the difference in sign of the crystalline field parameters in intermetallic compounds and dilute alloys. This difference is attributed to the much smaller screening effects in the former.

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TABLE 1

The crystalline field splitting ground state of rare earth ions in various dilute alloys and intermettallic compounds. The sign of the crystalline field parameters was deduced from ESR experiments as well as other experimental techniques.

rare-earth ion	host	structure	crystalline field ground state	possible sign of $A_4 <r^4>$	possible sign of $A_6 < r^6 >$	reference of *ESR* work	support of other experimental techniques
Er	LaSb	NaCl	$\Gamma_8^{(1)}(\times = 0.78)$	+	+	[9]	a
Er	LuSb	NaCl	$\Gamma_8^{(1)}(\times = 0.77)$	+	+	[9]	a
Er	LaBi	NaCl	$\Gamma_8^{(1)}(\times = 0.84)$	+	+	[9]	a
Er	LuBi	NaCl	$\Gamma_8^{(1)}(\times = 0.81)$	+	+	[9]	a
Dy	LaSb	NaCl	Γ_6	+	+	[9]	a
Ce	LaSb	NaCl	Γ_7	+	+	[9]	a
Yb	LaSb	NaCl	Γ_6	+	+	[9]	a
Yb	$LaPd_3$	Cu_3Au	Γ_7	−	− or +	[9]	b
Er	LaB_6	CsCl	Γ_6	+ or −	− or +	[9]	c
Er	Ag	fcc	Γ_7	−	+	[10]	d
Dy	Ag	fcc	Γ_7	−	+	[11]	d
Er	Au	fcc	Γ_7	−	+	[10]	d
Dy	Au	fcc	$\Gamma_8^{(1)}(\times = 0.85)$	−	+	[8]	d
Yb	Au	fcc	Γ_7	−	+	[10]	d
Er	Al	fcc	Γ_7	−	+	[12]	NONE
Dy	Al	fcc	Γ_7	−	+	[12]	«
Er	Th	fcc	Γ_7	−	+	[13]	«
Dy	Th	fcc	Γ_7	−	+	[13]	«
Er	Ir	fcc	Γ_7	−	+	[14]	«
Dy	Ir	fcc	Γ_7	−	+	[14]	«
Er	Rh	fcc	Γ_7	−	+	[15]	«
Dy	Rh	fcc	Γ_7	−	+	[15]	«
Er	Pt	fcc	Γ_6	−	+	[16]	«
Er	Pd	fcc	$\Gamma_8^{(3)}$	−	−	[17]	«
Dy	Pd	fcc	$\Gamma_8^{(3)}$	−	−	[18]	«

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TABLE II

The sing of $A_4 < r^4 >$ and $A_6 < r^6 >$ for the various cubic structures as expected according to the point charge model and 5d and f-like virtual bound states.

structure	effective charge on ligands	point charge		5d virtual bound state			f mixing
		sign of $A_4 < r^4 >$	sign of $A_6 < r^6 >$	VBS ground state	symmetry of VBS charge distribution	sign of $A_4 < r^4 >$	sign of $A_6 < r^6 >$
fcc (12)	+	+	+	$d\varepsilon$	fcc	−	−
fcc (12)	−	−	−	$d\gamma$	octahedron	+	+
octahedral, Nacl (6)	+	−	−	$d\gamma$	octahedron	+	+
« Nacl (6)	−	+	+	$d\varepsilon$	fcc	−	−
S. Cube, CsCl (8)	+	+	−	$d\varepsilon$	fcc	−	+
« CsCl (8)	−	−	+	$d\gamma$	octahedron	+	−