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Anomalous crystal-field splittings of lanthanide S-states in metals

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Compared are recent EPR, susceptibility, and neutron measurements of both S-state (b_4^0) and non-S-state ($A_4^0\langle r^4\rangle$) lanthanide-ion crystal-field splittings in metals. The ratio of the S-state to the non-S-state fields $\mathcal{R} = b_4^0/A_4^0\langle r^4\rangle$ in *some* metals is anomalously large and cannot be explained by the current insulator theory. We suggest that there must exist an extra "metallic" contribution to *both* $A_4^0\langle r^4\rangle$ and the ratio $\mathcal{R}$. The non-S-state field $A_4^0\langle r^4\rangle$ is divided into two: (i) all Coulombic and exchange contributions, and (ii) a covalent contribution similar to that found in insulators. We show that the latter term is more efficient in its contribution to the S-state field b_4^0. We suggest, in the anomalous metals, the S state b_4^0 is dominated by covalent mixing but that for the non-S-state ions there is a partial cancellation between covalent and the coulomb-field contributions. Finally the implications for the Gd^{3+}, $4f^7$ to $4f^8$ interconfigurational energy are explained.

I. INTRODUCTION

Recent electron-paramagnetic-resonance (EPR) measurements[1–5] show large crystal-field (fine-structure) splittings for the lanthanide S-state ions Gd^{3+} and Eu^{2+} as impurities in a number of metals and intermetallic compounds. Such splittings are found to be of the same order as, *but in some cases larger than*, similar splittings found in insulators.[6]

This at first would not be too surprising since it is believed that in insulators the S-state crystal field results from several processes of differing sign.[7,8] A not unreasonable shift in the resulting partial cancellation might explain the larger metallic splittings. These results only become surprising when they are compared with measurements on non-S-state lanthanide ions, e.g., Er^{3+}, Dy^{2+}, and Pr^{3+}, etc., in the same host materials.[9–12] Measurements on non-S-states can be viewed as being a direct measure of the fundamental crystal electric field. Such measurements show that, upon comparison of an insulator and a metal *with similar S-state splittings*, the fundamental crystal field *in the metal* can be as much as, or even more than, an order of magnitude smaller. Upon further analysis the difference between metals and insulators becomes even more surprising. The recent analysis by Newman and Urban[8,13] of insulator data indicates the plausibility, at the least, of proportionality between the S-state crystal field (b_4^0) and the fundamental crystal field ($A_4^0\langle r^4\rangle$), as seen by the non-S-state ions. In general, as explained by Newman and Urban, this analysis is complicated by questions of the local coordination near the impurity site, a problem compounded by the relatively complicated unit cells found for many of the more studied insulators and by questions involving the relative ionicity of the host ligands. However, for a series of isoelectronic simple cubic insulators, one might expect *at least* a strong correlation between the S-state splittings characterized by b_4^0 and the non-S-state splittings characterized by $A_4^0\langle r^4\rangle$. In Fig. 1 we compare the data for (Ca, Sr, and Ba)F (Refs. 6, 14) with data for the monopinictides, R(P, As, Sb, and Bi).[5,12] (R is a rare earth). To a much better degree than would be expected, for the insulator, CaF_2, series the Gd^{3+} (b_4^0) and Dy^{2+} ($A_4^0\langle r^4\rangle$) data are proportional, to within a few percent, with a ratio $\mathcal{R} = (b_4^0/A_4^0\langle r^4\rangle) = 2\times 10^{-5}$. In contrast the data for the monopinictides, e.g., LaP through LaBi, shows a strong anticorrelation between b_4^0 and $A_4^0\langle r^4\rangle$. The characteristic property of these systems, at least as it is evidenced by the EPR Korringa rate,[15] is the steady increase in metallic (or covalent) character in passing from RP to RBi. Thus while the RP results, corrected to the Dy^{3+} radial integral $\langle r^4\rangle$, have a ratio equal, within a factor of 2, to that for CaF_2, the more metallic RBi has a ratio about an order of magnitude larger. It would be wrong, however, to attribute this lack of proportionality between b_4^0 and $A_4^0\langle r^4\rangle$ solely to an increase in metallic character. The data for several cubic and axial metals, together with some comparative insulator

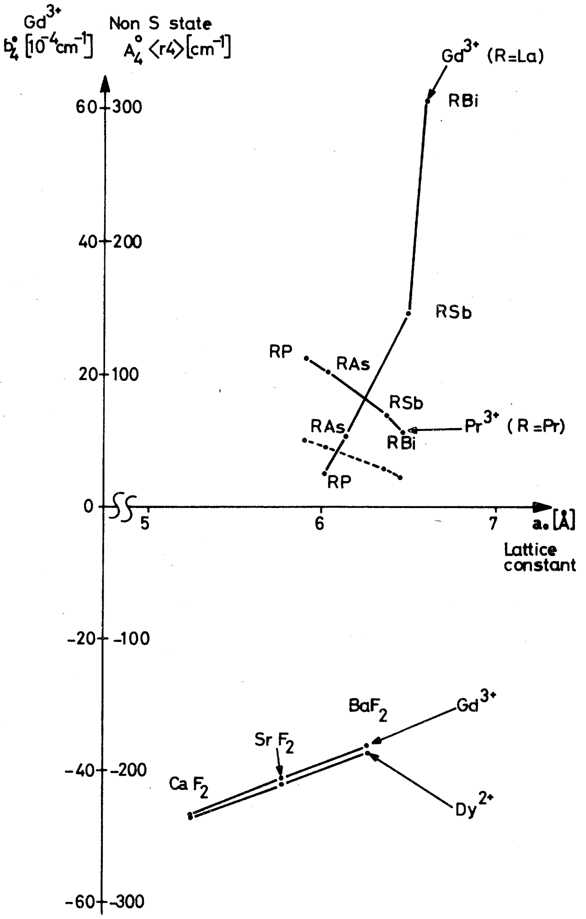

FIG. 1. Comparison of S-state and non-S-state crystal-field parameters for Ca, Sr, and Ba fluorides with those for the monopinictides. Data for the fluorides is taken from Ref. 6 and 14 and for the monopinictides from Ref. 5 and 12. The non-S-state data for the pinictides corresponds to the concentrated Pr^{3+} compounds PrP through PrBi, the dotted curve represents these results corrected to the Dy^{3+} $\langle r^4\rangle$. It is clear that while there is excellent correlations between b_4^0 and $A_4^0\langle r^4\rangle$ for the insulators, this is not so for the metallic pinictides.

data, are given in Table I. One sees that even for "good" metals such as the hexagonal metal sequence Sc, Y, and Lu or for the cubic metals Pt, Pd, Ag, and Au (b_4^0 for Au is a recently corrected value) there is again, if anything, an anticorrelation between b_2^0 or b_4^0 and $A_2^0\langle r^2\rangle$ or $A_4^0\langle r^4\rangle$.

The fact that makes these results quite mysterious is the size of the largest ratios $\mathcal{R}=|b_4^0/A_4^0\langle r^4\rangle|$; $\mathcal{R}=5.7\times10^{-4}$ for Pt. This is more than an order of magnitude larger than the largest insulator $\mathcal{R}$, that we have been able to find, namely $\mathcal{R}=2\times10^{-5}$ for CaF_2:Gd^{3+}. As we shall attempt to show in Sec. II, this ratio is limited, in its order of magnitude, by the size of the spin-orbit coupling parameter, $\zeta=0.21$ eV for Gd^{3+},[16] and the excitation energy, about 4 eV,[17] from the ground to first excited LS manifolds of the $4f^7$ configuration. Since both of these quantities, for a $4f$ shell, are determined principally by the impurity core potential the *individual contributions* to the ratio $\mathcal{R}$ should change very little from host to host be it an insulator or a metal. Our estimates presented in Sec. II make it very difficult to believe that this conventional spin-orbit coupling to excited LS manifolds is responsible for the S-state splittings in the most "anomalous" (largest $\mathcal{R}$) metals. It must be emphasized however that not all of the metals listed in the table are "anomalous." The S-state crystal-field splittings of Ag, Y, Lu and the two least metallic pinictides *might* be explained by the insulator processes alone. Only Pt, Pd, and Sc with Gd impurities and $LaAl_2$ with Eu^{2+} impurities are clearly anomalous.

We suggest that there must exist an extra "metallic" process, presumably involving the conduction electrons, and further, in view of the wide variation in $\mathcal{R}$, *that this process is extremely sensitive to the electronic structure of the impurity vis à vis that of the host metal.* A clue to the possible nature of such a process comes from a comparison of the EPR data[3] for Gd^{3+} and Eu^{2+} in $LaAl_2$. The Gd^{3+} crystal field is too small to be observed, which under the prevalent experimental conditions implies that $b_4^0<30\times10^{-4}$ cm^{-1}. This should be compared with the very large splittings, $b_4^0=102\times10^{-4}$ cm^{-1}, for Eu^{2+}; the largest in a metal to date. This ratio in b_4^0 parameters is in the wrong sense and much larger than would be expected upon the basis of the usual spin-orbit coupling.[18] Together with the slightly larger radial size of Eu^{2+}, an obvious difference between these two ions is the relative stability of the $4f^7$ configuration. The ion Eu^{2+} is much less stable as is perhaps evidenced, in $LaAl_2$ itself, by the smaller positive g shift, i.e., there is a larger negative covalent contribution, and in general by its tendency to form mixed and/or intermediate valence compounds. These facts suggest that in metals covalent mixing of the magnetic $4f$ electrons with the conduction electrons might play a role in the S-state splitting.

The principal purpose of this paper is to examine this crystal field role of covalent mixing. We show that in fact it does lead to a new "metallic" process for S-state splittings and further that it is very sensitive to the electronic structure of the impurity *vis à vis* that of the host. We also show that it is extremely important to distinguish between Coulombic and exchange contributions (CEC) (including screening) and covalent contributions to

TABLE I. In cases where the Eu^{2+} or Gd^{3+} b_4^0 data are given in Gauss we have used the nominal g value of 2.0 to convert to cm^{-1}.

Host	$A_2^0\langle r^2\rangle$ (cm^{-1})	$A_4^0\langle r^4\rangle$ (cm^{-1})	Ion	b_2^0 (10^{-4} cm^{-1})	b_4^0 (10^{-4} cm^{-1})	Ion	Ratio $\mathcal{R}$	Reference
$LaAl_2$		−40			102 <30	Eu^{2+} Gd^{3+}	-2.6×10^{-4} $\lvert\mathcal{R}\rvert < 7.6 \times 10^{-5}$	a, 3
Pt		−14 (or −30)	Er^{3+}		80	Gd^{3+}	-5.7×10^{-4}	10, 2
Pd		−20	Er^{3+}		27	Gd^{3+}	-1.35×10^{-4}	9, 1
Au		−22	Er^{3+}		28	Gd^{3+}	-1.27×10^{-4}	b, c
Ag		−46	Er^{3+}		7	Gd^{3+}	-1.5×10^{-5}	b, d
Mg	···			+130		Gd^{3+}	···	22
Sc	−15		Er^{3+}	−308		Gd^{3+}	2.05×10^{-3}	11, 4
Y	−85		Er^{3+}	−140		Gd^{3+}	1.6×10^{-4}	11, 4
Lu	−44		Er^{3+}	−58		Gd^{3+}	1.3×10^{-4}	11, 4
ThO_2		···			−56	Gd^{3+}	···	6
MgO		367	Er^{3+}		−35	Gd^{3+}	-9.5×10^{-6}	e, 6
CaF_2		−284	Gd^{3+} excited states		−46 −58	Gd^{3+} Eu^{2+}	1.6×10^{-5} 2.0×10^{-5}	19, 6 16
$LaCl_3$	94		Er^{3+}	16		Gd^{3+}	1.7×10^{-5}	16
Rare-earth ethyl sulphates	120		Er^{3+}	205		Gd^{3+}	1.7×10^{-4}	16

[a] M. Loewenhaupt and H. E. Heonig, Solid State Commun. 25, 197 (1978).

[b] G. Williams and L. L. Hirst, Phys. Rev. 185, 407 (1969).

[c] K. Baberschke (private communication); the original measurements [E. P. Chock, R. Chui, D. Davidov, R. Orbach, D. Shaltiel, and L. J. Tao, Phys. Rev. Lett. 27, 582 (1971)] correspond to $b_4^0 = -18 \times 10^{-4}$ cm.

[d] S. Oserhof, B. Gehmann, S. Schultz, and C. Rettori, Phys. Rev. Lett. 35, 679 (1975).

[e] D. Descamps and Y. Merle D'Aubigne, Phys. Lett. 8, 5, (1964).

the *fundamental* crystal field $A_4^0\langle r^4\rangle$. If both types of contribution are defined as entering the non-S-state $A_4^0\langle r^4\rangle$ with equal weightings, then they enter the S-state b_4^0 with different weightings or "efficiencies" and even different signs. This indicates that in metals the separation of covalent effects between $\mathcal{R}$ and $A_4^0\langle r^4\rangle$ is rather arbitrary and perhaps not very useful.

We suggest that in the anomalous metals there is a partial cancellation between the contributions to the non-S-state crystal field $A_4^0\langle r^4\rangle$ but that there is a single dominant covalent contribution to the S-state field b_4^0. This is the exact opposite of what is believed to be the case in insulators. There it is suggested,[8] there are important cancellation effects in the S-state rather than the non-

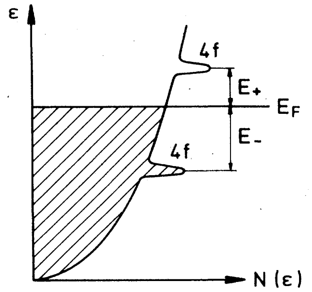

FIG. 2. Conventional Friedel-Anderson picture of a local moment. The energy E_+ is that required to add one electron to the $4f$ shell and E_- the energy required to remove one electron. Both of these energies are reduced considerably by screening effects, see text.

S-state field.

What emerges from analysis of the EPR data for Gd^{3+} in the anomalous metals Pt, Pd, and Sc is that the energy $E_+ = \epsilon_d + U$ in the usual Friedel-Anderson picture, see Fig. 2, is rather smaller, about 1–2 eV, than has hitherto be suspected, that is the energy difference between the configurations $4f^7$ and $4f^8$ (actually $4f^7 5d^{1+x}$ and $4f^8 5d^x$ when screening is included) is really quite small. We believe that if this is confirmed it would represent a significant shift in our understanding of lanthanide impurities in these metals.

In order to keep our development free from constant qualifications we shall specialize henceforth, unless stated otherwise, to cubic insulators or metals and to the S-state ion Gd^{3+}. We shall ignore the sixth-order parameter since there is relatively little reliable data available and because for an S-state such terms are of relatively little importance.

II. INSULATOR PROCESSES

In this section we wish to show that the processes usually suggested as to being responsible for the S-state splittings in insulators are too small to explain the most anomalous splittings in metals. Several processes may be involved, these have been discussed at some length by Wybourne[7] and by Newman and Urban.[8,13] *Here we concentrate upon the limitation, to the order of magnitude, implied by the size of the spin-orbit coupling and by the energy structure of the excited levels of the $4f^7$ configuration.* Our basic tenet is that these are determined principally by the impurity core potential and therefore will be expected to change little from host to host be it an insulator or a metal.

A. Direct field contribution (crystal field)

The unperturbed $4f^7$ ground state $|^8S_{7/2}\rangle$ has no nonzero crystal-field (CF) matrix elements; however, the spin-orbit interaction mixes excited ${}^{2J+1}L_S$ manifolds into the ground manifold. Wybourne[7,13] gives for the Gd^{3+} the ground vector

$$|^8\mathcal{S}_{7/2}\rangle = s\,|^8S_{7/2}\rangle + p\,|^6P_{7/2}\rangle + d\,|^6D_{7/2}\rangle + f\,|^6F_{7/2}\rangle + g\,|^6G_{7/2}\rangle\,, \tag{2.1}$$

where $s = 0.9866$, $p = 0.162$, $d = -0.0123$, $f = 0.0010$, and $g = -0.00014$. Appropriate to a cubic environment, the crystal field Hamiltonian is

$$V_{\rm cf} = 8A_4^0\langle r^4\rangle(4\pi/9)^{1/2}Y_4^0\,, \tag{2.2}$$

where the Y_l^m are normalized spherical harmonics. According to Newman[13] the nonzero contributions to $\langle ^8\mathcal{S}_{7/2}\| V_{\rm cf}\| ^8\mathcal{S}_{7/2}\rangle$ involve $\langle ^6P_{7/2}\| V_{\rm cf}\| ^6G_{7/2}\rangle$ and therefore the small product $pg = -2.28\times10^{-5}$, or $\langle ^6D_{7/2}\| V_{\rm cf}\| ^6F_{7/2}\rangle$ and the product $df = -1.23\times10^{-5}$. Taking as an estimate for the *size* of the relevant Stevens' factor $\beta \equiv \langle l\,\|\beta\|\,l\rangle = 2/11.45 = 4.04\times10^{-3}$ and remembering the factor of 60 involved in the definition of b_4^0 gives

$$pg(\pm\beta)A_4^0\langle r^4\rangle = b_4^0/60\,, \tag{2.3a}$$

that is

$$|\mathcal{R}| = |b_4^0/A_4^0\langle r^4\rangle| = -60pg\beta = 5.49\times10^{-6}\,, \tag{2.3b}$$

while for the df process $|\mathcal{R}| = 2.98\times10^{-6}$. As a direct check upon this estimate, it might be compared with the combined pg and df ratio obtained directly by O'Hare and Dolan,[19] who show, for CaF_2, a crystal field of $A_4^0\langle r^4\rangle = 284$ cm^{-1}, chosen to fit excited-state data, results in a ground state splitting corresponding to $b_4^0 = -2\times10^{-3}$ cm^{-1}, i.e., $|\mathcal{R}| = 7.04\times10^{-6}$. Such relatively good agreement lends support to our other estimates below.

B. Relativistic crystal field (RCF)

For nonrelativistic wave functions the matrix elements $\langle ^8S_{7/2}\| V_{\rm cf}\| ^6F_{7/2}\rangle$ are zero. Including relativistic effects[13] results in a contribution proportional to $sf = 9.9\times10^{-4}$ times *small* relativistic differences in the radial integrals $\langle r^4\rangle$, implying an additional small factor of 2.2×10^{-2}.[8] Our estimate for this process is therefore $|\mathcal{R}| = 5.28\times10^{-6}$.

Qualitatively, both of the above processes involve coefficients and radial integrals determined principally by the impurity potential, and therefore, they will change little from host to host, be it an insulator or a metal. Quantitatively, even combined, these are simply too small to explain ratios as large as $\mathcal{R}_{\rm Pt} = 5.7\times10^{-4}$.

C. Correlation crystal field (CCF)

A further process, suggested by Rajnak and Wybourne,[20] is the *intra-atomic* configuration mixing of $4f^7$ and $4f^6 6p$ or $4f^6 5f$. This involves[13] the products $pf = 1.62\times10^{-4}$ or $d^2 = 1.51\times10^{-4}$ times a small parameter associated with the configuration mixing. Qualitatively this process will differ in metals; the $6p$ and to a less extent the $5f$ orbitals become hybridized into the s-p conduction band. However, the products pf and d^2 imply $|\mathcal{R}| < 7.59\times10^{-5}$ which without accounting for an additional smallness parameter is almost an order of magnitude too small.

We conclude that, unless the Gd^{3+} ground-state vector is *radically* altered, these insulator processes are very much too small to explain the observed ratios $|\mathcal{R}| = |b_4^0/A_4^0\langle r^4\rangle|$ in the most anomalous metals. Our estimates *are* consistent with the maximum observed insulator ratios, i.e., the case of least cancellation. In the CaF_2 series

$\mathcal{R} \sim 1.5 \times 10^{-5}$ corresponding roughly to the sum of the first two processes.

We finally remark that the actual calculation of $\mathcal{R}$, rather than its maximum order of magnitude, is a very difficult task which we have avoided. The difficulties involved are illustrated by the fact that the experimental ratios $\mathcal{R}$, for different insulators, can be of differing signs; this indicating strong cancellation effects *in the S-state crystal field* (see Refs. 8 and 13).

III. METAL PROCESSES

The characteristic property of a metal is the partially filled conduction band. It is natural, therefore, to look for an additional process involving these electrons.

The principal interaction between the magnetic $4f^7$ electrons and the conduction electrons is the $J\vec{S}\cdot\vec{s}$ exchange interaction. Smith[21] has attempted to explain metallic splittings involving this and the spin-orbit interactions *in the host*. In the context of the systems Pt, Pd, Ag, and Au and for the monopinictides this is an attractive proposition. The crystal field parameter b_4^0 is larger for the heavier host elements, corresponding, correctly, to the larger spin-orbit coupling in the host. Unfortunately, by the same token the systems Sc, Y, and Lu form a counterexample. However, on a more basic level this process cannot offer a satisfactory explanation. The values of the effective exchange J for the $3d$ S-state ion Mn^{2+} are perhaps an order of magnitude larger than the values for $4f$ ions. Since the axial parameter b_2^0 involves the second power of ρJ, ρ the density of states, it is implied that $3d$ S-state splittings should be more than an order of magnitude larger than those for $4f$ ions. In fact the Mg:Gd^{3+} splitting,[22] $b_2^0 = 130 \times 10^{-4}$ cm^{-1}, is larger than that[23] for Mg:Mn^{2+}, $b_2^0 = 65 \times 10^{-4}$ cm^{-1}.

A related interaction to the exchange interaction is the covalent mixing of the $4f$ electrons with the conduction electrons; it is this which is responsible for the large, negative, effective exchange interaction for $3d$ ions. Schrieffer and Wolff[24] have calculated this effective exchange within the Anderson model, the resulting covalent mixing (cm) exchange constant J_{cm} is (for notation see Sec. IV)

$$J_{cm} = |V_{kf}|^2 (1/E_- - 1/E_+) , \tag{3.1}$$

where in the familiar picture, see Fig. 2, $E_- \equiv \epsilon_d$ is the energy required to promote a $4f$ electron to the Fermi surface and $E_+ = \epsilon_d + U$ is the energy required to add an electron from the Fermi surface, to the $4f$ orbital. It is important to the present discussion to realize that both of these energies are considerably modified by screening as described by Herbst *et al.*[25]; we shall return to this question in Sec. VI. Involved in this effective exchange interaction are two virtual processes in which the $4f^7$ shell changes its configuration, or valence, to become either $4f^6$ or $4f^8$. Since neither of these latter two configurations correspond to an S state, during these "virtual valence fluctuations" the impurity becomes directly sensitive to the crystal field. It is this process of S-state splitting by virtual valence fluctuation which we wish to discuss for the remainder of this paper.

Although again the role of covalent mixing is known to be greater for the $3d$ ion Mn^{2+}, the basically different electronic structure of $3d$ ions leaves open the possibility of reconciling $3d$ and $4f$ splittings. Thus while for the $3d$ series the crystal-field splitting often exceeds the spin-orbit splitting, the inverse is true for the $4f$ ions. Therefore, although the $3d^5$ configurations will undergo more easily valence fluctuations, the non-S-state configurations to which they fluctuate can have their angular momentum quenched and thereby cause no fine-structure splittings.

For the remainder of this section we give a sketch of the principles involved in this fluctuation process, the more rigorous, but less transparent derivation is given in Sec. IV.

Schematically one might represent these valence fluctuations by a wave function

$$\Phi_{4f7} = \phi^0_{4f^7} + a\phi^0_{4f^8} + b\phi^0_{4f^6} . \tag{3.2a}$$

If the conduction electron which is added to or taken from the $4f^7$ configuration has a wave vector k then one has from elementary perturbation theory that

$$a = N^{-1/2} V^*_{kf} / (E_+ - \epsilon_k) \tag{3.2b}$$

and

$$b = N^{-1/2} V_{kf} / (\epsilon_k - E_-) . \tag{3.2c}$$

Summing over all allowed k, i.e., electrons below E_F for the change $4f^7 \to 4f^8$, etc. then the matrix elements of the crystal field $\langle \phi^0_{4f^8} \| V_{cf} \| \phi^0_{4f^8} \rangle$ will have a coefficient

$$A_+ = N^{-1} \sum_{k<k_F} \frac{|V_{kf}|^2}{(E_+ - \epsilon_k)^2} . \tag{3.3a}$$

and for $\langle \phi^0_{4f^6} \| V_{cf} \| \phi^0_{4f^6} \rangle$ the coefficient

$$A_- = N^{-1} \sum_{k>k_F} \frac{|V_{kf}|^2}{(E_- - \epsilon_k)^2} . \tag{3.3b}$$

The "admixture parameters"[26] $A_\pm$ correspond to the fractional admixture of $4f^8$ and $4f^6$ into $4f^7$.

However, it is clear that a scalar mixing interaction acting upon an S-state wavefunction cannot alone produce a crystal-field splitting; the spin-orbit splitting of the LS ground manifold of the virtual $4f^6$ and $4f^8$ configurations must be accounted for. The energy of such ${}^{2J+1}L_S$ states is determined by the total angular momentum J. Thus $E_\pm$ and $A_\pm$ become functions of J:

$$A_\pm(J)=\sum_k |V_{kf}|^2 \frac{\pm(n_k-\frac{1}{2}\pm\frac{1}{2})}{[E_\pm(J)-\epsilon_k]^2}\,, \tag{3.4}$$

where n_k is the usual fermion occupation factor. It is the differences between the $A_\pm(J)$ which determines the crystal field parameter b_4^0. The full calculation has one further complication, namely, that it is necessary to account for interference between the processes for the different ${}^{2J+1}L_S$ states. This is postponed until Sec. IV.

The minimum denominator in (3.4) is $[E_\pm(J)]^2$, hence the $E_\pm$ are the key parameters of the theory. As with the insulator processes we are using the spin-orbit coupling to admix crystal field splitting into the S state. Only if one of the excitation energies $E_\pm$ is less than that for the insulator processes (~4 eV) can the new process possibly be more effective than those already discussed. This is the basic problem; in order to explain the anomalously large ratios $\mathcal{R}$ in metals one needs some very low-lying excited states which have nonzero angular momentum.

IV. CALCULATION

Since it is more familiar, here we shall perform the calculation using the Schrieffer-Wolff transformation. However, the calculation may also, and was first, performed using the new Feynman diagram method for the Anderson model developed by one of the authors.[26]

We write the Anderson model[27] in the form

$$H=H_{\text{cond}}+H_{\text{ion}}+H_1\,, \tag{4.1a}$$

where

$$H_{\text{cond}}=\sum_{k,\sigma}\epsilon_k\hat{n}_{k\sigma}\,, \tag{4.1b}$$

$$H_1=N^{-1/2}\sum_{k,m,\sigma}(V_{fk}c^\dagger_{km\sigma}c_{m\sigma}+V^*_{fk}c^\dagger_{m\sigma}c_{km\sigma})\,, \tag{4.1c}$$

and

$$\begin{aligned}H_{\text{ion}}=&\sum_{m\sigma}\epsilon_d\hat{n}_{m\sigma}+U\sum_{m,m'}\hat{n}_{m\uparrow}\hat{n}_{m'\downarrow}\\&+(U-J)\sum_{\sigma,m>m'}c^\dagger_{m\sigma}c_{m\sigma}c^\dagger_{m'\sigma}c_{m'\sigma}\\&+V_{\text{cf}}+\zeta\sum_i\vec{1}_i\cdot\vec{s}_i\equiv H_{00}+V_{\text{cf}}+H_{\text{so}}\,,\end{aligned} \tag{4.1d}$$

where in addition to the usual Anderson model we have included the crystal-field V_{cf} and spin-orbit coupling $H_{\text{so}}=\zeta\sum_i\vec{1}_i\cdot\vec{s}_i$.

Using the Schrieffer-Wolff transformation,[28] H_1 is eliminated and replaced by a new term H_2 whose matrix elements are

$$\langle b|H_2|a\rangle=\frac{1}{2}\sum_c\langle b|H_1|c\rangle\langle c|H_1|a\rangle \times\left(\frac{1}{E_a-E_c}+\frac{1}{E_b-E_c}\right). \tag{4.2a}$$

Specializing to diagonal matrix elements one can write

$$\langle a|H_2|a\rangle=\sum_c\langle a|H_1|c\rangle\frac{1}{E_a-E_c}\langle c|H_1|a\rangle \equiv\langle a|H_1\frac{1}{E_a-H_0}H_1|a\rangle\,. \tag{4.2b}$$

We are interested in diagonal impurity crystal-field matrix elements. We take $|a\rangle$ to be the maximal spin state of the impurity times a typical Fermi sea for a temperature T:

$$|a\rangle=\prod_{m=-3}^{3}c^\dagger_{m\uparrow}|T\rangle\,. \tag{4.3}$$

We assume a finite temperature in order to avoid technical problems associated with the Kondo divergence. We also need two intermediate states connected to $|a\rangle$ via H_1; these are

$$|k,1\rangle=c^\dagger_{m\downarrow}c_{km\downarrow}|a\rangle \tag{4.4a}$$

corresponding to an impurity configuration $4f^8$ and

$$|k,2\rangle=c^\dagger_{km\uparrow}c_{m\uparrow}|a\rangle \tag{4.4b}$$

corresponding to $4f^6$. It follows that, e.g.,

$$\langle k,1|H_1|a\rangle=N^{-1/2}V^*_{fk}n_{km\downarrow}\,, \tag{4.5}$$

where $n_{km\sigma}=1$ or 0 depending on whether in $|T\rangle$ the level $km\sigma$ is occupied or not.

Required is a term linear in the crystal field; retaining only this:

$$\langle a|H_2|a\rangle=\langle a|H_1\frac{1}{E_a-(H_{\text{cond}}+H_{00}+H_{\text{so}})} \times V_{\text{cf}}\frac{1}{E_a-(H_{\text{cond}}+H_{00}+H_{\text{so}})}H_1|a\rangle\,. \tag{4.6}$$

The final step is to include suitable complete sets of states. One has that the $|k,i\rangle$ are eigenstates of S, S_z, L, and L_z, namely,

$$|k,1\rangle\equiv|4f^8;\ S=3,\ S_z=3,\ L=3,\ L_z=m\rangle|T\rangle \tag{4.7a}$$

and

$$|k,2\rangle\equiv|4f^6;\ S=3,\ S_z=3,\ L=3,\ L_z=-m\rangle|T\rangle\,. \tag{4.7b}$$

Between these states V_{cf} (but not H_{so}) is diagonal. The diagonal states for $H_{00}+H_{\text{so}}$ are

$$|d\rangle \equiv |4f^8;\ L,\ S;\ J,\ J_z\rangle\,|T\rangle \tag{4.8a}$$

and

$$|e\rangle \equiv |4f^6;\ L,\ S;\ J,\ J_z\rangle T\rangle\,, \tag{4.8b}$$

i.e., one has

$$(H_{00}+H_{\text{so}}-E_a)\,|d\rangle=[E_+-(\zeta/2S)J(J+1)]\,|d\rangle \equiv E_+(J)\,|d\rangle \tag{4.9a}$$

and

$$(H_{00}+H_{\text{so}}-E_a)\,|e\rangle=[E_-+(\zeta/2S)J(J+1)]\,|e\rangle \equiv E_-(J)\,|e\rangle\,, \tag{4.9b}$$

retaining above only the J-dependent spin-orbit terms in $E_\pm(J)$. Now since $|a\rangle$ is the maximal spin state the Wigner-Eckart theorem implies that the left-hand side of Eq. (4.6) is proportional to $O_4^0(S_z=\frac{7}{2})=420$.

$$\langle a|H_2|a\rangle=(b_4^0/60)O_4^0(S_z=\tfrac{7}{2})=7b_4^0\,. \tag{4.10}$$

Whence inserting the above complete sets of states into Eq. (4.11) we obtain the general result:

$$\frac{b_4^0}{A_4^0\langle r^4\rangle}=\frac{1}{7}\sum_{k,\pm J,J'}|V_{kf}|^2\frac{1}{E_\pm(J)-\epsilon_k}\,\frac{1}{E_\pm(J')-\epsilon_k} \times[\pm(n_k-\tfrac{1}{2}\pm\tfrac{1}{2})] \times\sum_{m,m'}M(J;m,m')[\pm\beta O_4^0(m')] \times M(J';m,m')\,, \tag{4.11a}$$

where

$$M(J;m,m')=\langle S=3,\ L=3;\ S_z=3,\ L_z=m\,|L,\ S;\ J,\ J_z=3+m\rangle \times\langle S=3,\ L=3, S_z=3+m-m',\ L_z=m'\,|L,\ S;J,J_z=3+m\rangle \tag{4.11b}$$

involves the Clebsch-Gordan coefficients $\langle S,L;S_z,L_z|L,S;J,J_z\rangle$ and here the operator $O_4^0(m)$ takes the values appropriate to $l=3$. This expression may be thermally averaged over the conduction electron, states $|T\rangle$ whence $n_k=(e^{\beta\epsilon_k}+1)^{-1}$, $\beta=1/kT$. For the second-order ratio $b_2^0/A_2^0\langle r^2\rangle$ one simply replaces β by α and 4 by 2 everywhere in Eq. (4.11). Note that β is positive while α is negative.[16]

There is one simple limit of the expression, i.e., when $\zeta>E_+$ then

$$b_4^0=(0.042)A_+(J=6)A_4^0\langle r^4\rangle\,. \tag{4.12}$$

A similar expression will be valid for Eu^{2+} in systems where the impurity is close to a valence change, $\text{Eu}^{2+}\rightarrow\text{Eu}^{3+}$ as, for example, in $\text{EuPt}_{2-x}\text{Rh}_x$.[29] In such a case it is E_- which is small and therefore the admixture parameter A_- which is large, perhaps a few times $\frac{1}{10}$, whence Eq. (4.11) would predict a ratio some ten times larger than that for the most anomalous metals observed to date, and even larger (see Sec. V) if covalent terms in $A_4^0\langle r^4\rangle$ dominate!

A more useful expression, valid in the opposite limit $\zeta<E_\pm$ and which avoids Clebsch-Gordan coefficients, may be obtained as follows. One starts again with

$$\langle a|H_2|a\rangle=\langle a|H_1\frac{1}{E_a-(H_{\text{cond}}+H_{00}+H_{\text{so}}+V_{\text{cf}})}H_1|a\rangle \tag{4.13}$$

and expands in $(H_{\text{so}}+V_{\text{cf}})$. The first linear nonzero term arises in the fifth order. This term is

$$\langle a|H_2|a\rangle=\langle a|H_1[V_{\text{cf}}(H_{\text{so}})^4]_{\text{perm}} \times\left(\frac{1}{E_a-(H_{\text{cond}}+H_{00})}\right)^6 H_1|a\rangle\,, \tag{4.14}$$

where $[V_{\text{cf}}(H_{\text{so}})^4]_{\text{perm}}$ means the sum over all five permutations of H_{so} and V_{cf}. Now if

$$|a\rangle=|S=\tfrac{7}{2},\ S_z,\ L=0\rangle\,|T\rangle \tag{4.15}$$

it follows that

$$H_1|a\rangle=N^{-1/2}V_{kf}\sum_m(a^{1/2}|S=3,\ S_z-1,\ L=3,\ m\rangle +b^{1/2}|S=3,\ S_z+1,\ L=3,m\rangle)\,|T\rangle\,, \tag{4.16}$$

i.e., there is always a trace over the angular-momentum space, and as a result all of the above permutations are equal.

In principle the procedure is to evaluate $\text{Tr}_L[V_{\text{cf}}(H_{\text{so}})^4]$, which should be proportional to $O_4^0(S^z)$. In fact we need evaluate only the coefficient of $(S^z)^4$, which has a coefficient of 35 in $O_4^0(S_z)$. We obtain

$$\text{Tr}_L[V_{\text{cf}}(H_{\text{so}})^4]=(\zeta/2S)^4\tfrac{35}{8}(S_z)^4 \times\text{Tr}_L[O_4^0(m)m^4]A_4^0\langle r^4\rangle(\pm\beta)+\dots\,, \tag{4.17}$$

where the sign of β is determined by the configuration, $4f^8$ or $4f^6$, involved. Note though, that because it is sandwiched between two H_1 terms, the S_z belongs to an $S=3$ space and not the $4f^7$, $S=\frac{7}{2}$ space. We use the Wigner-Eckart theorem again and evaluate both sides for maximal spin. The result is

$$\frac{b_4^0}{A_4^0\langle r^4\rangle}=\sum_{\pm}\left\{\frac{5\times(60)^2\times 99}{7}\beta\left(\frac{\zeta}{6}\right)^4 \times\sum_k\left[\frac{|V_{kf}|^2}{N}\frac{(n_k-\frac{1}{2}\pm\frac{1}{2})}{(E_\pm-\epsilon_k)^6}\right]\right\}. \tag{4.18}$$

Evaluating this expression for a constant density of states gives

$$b_4^0=\sum_{\pm}\pm\tfrac{10}{63}(\zeta/E_\pm)^4[A_\pm(A_4^0\langle r^4\rangle)], \tag{4.19}$$

where $A_\pm=\rho|V_{fk}|^2/|E_\pm|\simeq-\rho J_{\mathrm{cm}}$. *This rough equality, that the largest* $A_\pm\simeq-\rho J_{\mathrm{cm}}$, *implies that the fractional admixture parameters* $A_\pm$ *may be estimated from the negative covalent contributions to the effective exchange.*

So far it has been assumed that all contributions to $A_4^0\langle r^4\rangle$ are of a Coulombic (plus screening, plus exchange), CEC type; no explicit account has been taken of any covalent contributions to $A_4^0\langle r^4\rangle$. The determination of this CEC alone is complicated. Various contributions can be identified.

(i) From the point charge of the ligand nuclei screened by the spherically symmetric core electrons.

(ii) Contributions from the s-p and d-band conduction electrons. In a free-electron picture the conduction electrons would have a uniform charge and therefore would not contribute to $A_4^0\langle r^4\rangle$. However, in real metals the band mass m_b of the s-p electrons is usually somewhat different from the free-electron mass m_e. If $m_b>m_e$ as in Zn and possibly Mg the conduction electrons are more concentrated in the core region. This leads to a small *screening* of the ligand charge given by (i). In contrast, in the transition metals orthogonality to the d band requires the s-p electrons to move away from the core region, $m_b>m_e$ and there will be an *antiscreening* effect, as has been suggested previously. The d band invariably has $m_b>m_e$, the d electrons can almost be classed as belonging to the core, and will therefore strongly *screen* the ligand charge. Such screening arguments suggest that in the noble and d-band metals there is a positive ligand charge roughly equal to the number of s-p conduction electrons, but enhanced, by say 10%–50%, because of antiscreening effects of the s-p conduction electrons.

(iii) However, the charge distribution within the *impurity* Wigner-Sietz cell will respond to the host ligand charge (and covalent mixing with the ligands) and this can lead to screening or even *overscreening* of the host ligands. Such an overscreening has been suggested by Coles and Orbach,[30] to explain the apparent negative ligand charge in the noble metals. The $5d$ electrons deform creating a greater negative charge in the regions adjacent to the positive ligands. This negative charge is closer to the impurity magnetic $4f$ electrons than the positive charge of the ligands and under suitable circumstances may dominate. In estimating this $5d$ contribution it is important to account for both direct Coulomb and exchange contributions. Chow[31] calculated that, for a strongly polarized $5d$ virtual bound state, VBS, the exchange contribution cancels 85% of the direct Coulomb contribution to the fourth-order field $A_4^0\langle r^4\rangle$. However, Eagles[32] has claimed for a weakly polarized $5d$ VBS, there is no such strong cancellation effect.

It may also be the case that the importance of this overscreening in the noble metal alloys has been overestimated. First, if Chow's exchange correction is used or if following Eagles the VBS is weakly polarized, then this contribution will not be very large. Second, in CsCl-structure systems—ErM(M = Rh, Pt, Cu, Ag, or Zn) $A_4^0\langle r^4\rangle$ is again large and negative—however, both the ligand charges *and the 5d contribution* are positive.[33] Here the large negative fields, in, e.g., ErAg, $|A_4\langle r^4\rangle|=-82$ °K (-56 cm^{-1}), must come from some other source, possibly covalent mixing.

A complication arises when comparing this screening effect that these $5d$ electrons have upon $A_4^0\langle r^4\rangle$ and b_4^0. As is explained in Sec. VI, during the configuration change $4f^7\rightarrow 4f^8$, which gives the dominant contribution to $\mathcal{R}$, most or all of the $5d$ electrons will be lost. *As a consequence, if* $5d$ *overscreening of* $A_4^0\langle r^4\rangle_{\mathrm{CEC}}$ *occurs for the non-S-state, it is most probably absent for the S state.*

(iv) Further complications can arise, for example, in a d-band metal. Besides the monopole contribution (ii), there will be multipole terms arising from the nonspherical distribution of charge within *ligand* cells.

To all of these CEC contributions to $A_4^0\langle r^4\rangle$ must be added to any covalent contribution. Thus covalency can enter *both* the theory for $A_4^0\langle r^4\rangle$ *and* the ratio $\mathcal{R}$. *In fact,* the ratios $\mathcal{R}$ for the CEC and the covalent terms are different; the addition theory is developed in Sec. V.

V. COVALENT CONTRIBUTIONS TO $A_4^0<r^4>$

It has been speculated[12] for some time that there might be important covalent contributions to the non-S-state crystal field $A_4^0\langle r^4\rangle$. The purpose of this section is to calculate within the Anderson model, the covalent contribution to $A_4^0\langle r^4\rangle$ and then to investigate the effect such contributions have upon the theory for $\mathcal{R}$ (or b_4^0). *We show that the covalent contribution to* $A_4^0\langle r^4\rangle$ *is sizable and that the corresponding contribution probably dominates* b_4^0.

Consider the crystal field seen by a single $4f$ electron, corresponding, in principle, to Ce^{3+}. The covalent contribution can be obtained, with suitable states $|a\rangle$, from (4.2b). It may be written as an angular-momentum (m) dependent energy,

$$\begin{aligned}\Delta\epsilon(m,\sigma) &= \frac{1}{N}\sum_{\substack{m',\sigma'\neq m,\sigma\\ \vec{k}}} |V_{m'\vec{k}}|^2 \frac{n_{\vec{k}}}{\epsilon_{\vec{k}}-E_+} + \frac{1}{N}\sum_{\vec{k}} |V_{m\vec{k}}|^2 \frac{1-n_{\vec{k}}}{E_- - \epsilon_{\vec{k}}}\\ &= \Delta\epsilon_0 - \frac{1}{N}\sum_{\vec{k}} |V_{m\vec{k}}|^2 \frac{n_{\vec{k}}}{\epsilon_{\vec{k}}-E_+} + \frac{1}{N}\sum_{\vec{k}} |V_{m\vec{k}}|^2 \frac{1-n_{\vec{k}}}{E_- - \epsilon_{\vec{k}}}\,, \end{aligned} \tag{5.1}$$

which *lowers* the energy of the $4f$ orbital, where the second line is obtained by adding and subtracting the restriction in the first sum and the first line. In the second line, the second term corresponds to an *antibonding* effect with those occupied conduction-electron states below the Fermi surface, while the last term corresponds to *bonding* effects with the vacant states above the Fermi surface. In this way the present theory resembles the insulator theory for $3d$ ions as described by Owen and Thornley.[34] In its full generality (5.1) represents a formidable problem; its evaluation requires a detailed knowledge of both the band structure and wave functions of the host. It is perhaps useful though to develop (5.1) a little further in analogy with the insulator theory.

Instead of states with definite angular momentum the $4f$ states may be constructed as "cubic harmonics." For $L=3$ these are characterized by Γ_2, Γ_4, and Γ_5 (see Ref. 16, p. 857). The splitting Δ_{45} between the Γ_4 and Γ_5 states is then given by an expression of the form

$$\begin{aligned}\Delta_{45} = &+\sum_{\vec{k}}[\alpha_5^+(\vec{k}) - \alpha_4^+(\vec{k})](\epsilon_{\vec{k}} - E_+)\\ &-\sum_{\vec{k}}[\alpha_5^-(\vec{k}) - \alpha_4^-(\vec{k})](E_- - \epsilon_{\vec{k}})\,,\end{aligned} \tag{5.2}$$

where

$$\alpha_\Gamma^\pm(\vec{k}) = (|V_{\Gamma\vec{k}}|^2/N)[\pm(n_{\vec{k}} - \tfrac{1}{2} \pm \tfrac{1}{2})]/(\epsilon_{\vec{k}} - E_\pm)^2.$$

The $\alpha_\Gamma^\pm$ parameters play the same role as the α_σ and α_π in the paper of Owen and Thornley.[34] The principal difference here is that it has been necessary to account for the energy dispersion of the ligand states. [The superscript (±) denotes antibonding or bonding.] Whether the difference $\alpha_5 - \alpha_4$) is positive or negative, which in turn determines the sign of $(A_4^0\langle r^4\rangle)_{\text{cov}}$ due to covalent mixing, depends upon two considerations: (i) the overlap of the Γ_4 or Γ_5 orbitals at the ligands; and (ii) the symmetry of the ligand wave function labeled $\vec{k}$. Thus, for example, because it points in that direction a Γ_4 orbital might have the largest amplitude at the ligand; however, if the symmetry of the relevant $\vec{k}$ state is close to Γ_5, the Γ_4 overlap will be zero, and it will be the case that $\alpha_5 > \alpha_4$. Notice that the covalent contribution to $A_4^0\langle r^4\rangle$ is sensitive to conduction electron states within an energy $E_\pm$ of the Fermi surface.

Returning to (5.1), in order to obtain a rough estimate for the maximum contribution to $(A_4^0\langle r^4\rangle)_{\text{cov}}$ it is assumed that $|V_{mk}|^2$ is roughly zero for some m. Because of the very strong distance dependence of the relevant overlaps this will not be a gross over-estimate. With this (5.1) becomes, dropping the constant $\Delta\epsilon_0$,

$$\Delta\epsilon = \frac{1}{N}\sum_{\vec{k}}\left(1 \pm \frac{O_4^0(m)}{320}\right)|V_{f\vec{k}}|^2 \times\left(-\frac{n_{\vec{k}}}{\epsilon_{\vec{k}} - E_+} + \frac{1-n_{\vec{k}}}{E_- - \epsilon_{\vec{k}}}\right), \tag{5.3}$$

where the arbitrary sign represents the actual uncertainty in the sign of this contribution. The integral over energy is estimated with a constant $|V_{f\vec{k}}|^2 = V^2$ and a square band, with density of states ρ width $2D$ and centered about the Fermi level. This gives

$$\begin{aligned}320\beta(A_4^0\langle r^4\rangle)_{\text{cov}} &\equiv 320\beta[(A_4^0\langle r^4\rangle)_{\text{cov}}^+ + (A_4^0\langle r^4\rangle)_{\text{cov}}^-]\\ &= \pm(b_+A_+E_+ - b_-A_-|E_-|)\,,\end{aligned} \tag{5.4}$$

where $b_\pm = \ln[(D + |E_\pm|)/|E_\pm|]$ is a factor determined by the shape of the band. Apart from these band factors $b_\pm$, (5.4) is of the same general form as (5.2), or the insulator expressions.

For a square d band just below the Fermi surface, corresponding to Pt or Pd, the A_- process is absent; with $2D = 5$ eV, $E_+ = 1$ eV, $\rho = 1$ state/(eV atom spin) and $V = 0.1$ eV (discussed in Sec. VI)

$$(A_4^0\langle r^4\rangle)_{\text{cov}} \sim \pm(10\text{ meV or }100\text{ cm}^{-1})\,. \tag{5.5}$$

One must expect covalent contributions which are of the same order as the experimentally observed values for $A_4^0\langle r^4\rangle$.

It is relatively straightforward to obtain the corresponding contribution to b_4^0. The calculation is similar but *not* identical to that presented in Sec. IV. Specializing to the limit $\zeta < |E_\pm|$, the equivalent of (4.14) is

$$\langle a|H_2|a\rangle = \langle a|H_1(H_{\text{so}})^4\left(\frac{1}{E_a-(H_{\text{cond}}+H_{00})}\right)^5 H_1|a\rangle\,. \tag{5.6}$$

For the maximal spin state using the approximation which leads to (5.3) (taking the negative sign):

$$\frac{b_4^0}{60}b_4^0O_4^0(\tfrac{7}{2}) = \langle S=3,\ S_z=3|\sum_{\vec{k},\pm}\frac{(V_{fk})^2}{N}\frac{(n_{\vec{k}}-\frac{1}{2}\pm\frac{1}{2})}{(E_\pm-\epsilon_{\vec{k}})^5}\ \mathrm{Tr}_L\left(\frac{O_4^0(m)}{320}(H_{\text{so}})^4\right)|S=3,\ S_z=3\rangle\,, \tag{5.7}$$

which gives, equivalent to (4.18),

$$b_4^0 = \sum_\pm +\left[\frac{(60)^2\times 99}{7}\left(\frac{\zeta}{6}\right)^4\frac{1}{320}\right.$$

$$\left.\times\sum_{\vec{k}}\frac{|V_{fk}|^2}{N}\frac{(n_{\vec{k}}-\frac{1}{2}\pm\frac{1}{2})}{(E_\pm-\epsilon_{\vec{k}})^5}\right]. \tag{5.8}$$

Using the constant density of states approximation gives

$$b_4^0 = \sum_\pm \mp\frac{10}{63}\left(\frac{\zeta}{E_\pm}\right)^4\left(\frac{1}{b_\pm 4}(A_4^0\langle r^4\rangle)_{\text{cov}}^\pm\right). \tag{5.9}$$

Combining this with the CEC results in the final expression

$$b_4^0 = \sum_\pm \pm\frac{10}{63}\left(\frac{\zeta}{E_\pm}\right)^4\left[A_\pm(A_4^0\langle r^4\rangle)_{\text{CEC}}\right.$$

$$\left.-\frac{1}{4b_\pm}(A_4^0\langle r^4\rangle)_{\text{cov}}^\pm\right], \tag{5.10}$$

where for the second order field 4 → 2 and $\frac{10}{63}\to -\frac{1}{3}$ (note: $\langle l\|\alpha\|l\rangle$ is negative). *Not only do the Coulomb and covalent terms enter with weights which differ by* $4b_\pm A_\pm$, *but they actually have differing signs.* Typically $4b_\pm A_\pm \ll 1$, hence covalent contributions to $A_4^0\langle r^4\rangle$ are much more "efficient" in causing S-state crystal-field splittings and will most probably dominate.

Finally, it should be noted that constant-density expressions (5.9) and (5.4) are misleading in one important aspect. Direct examination of (5.8) shows that b_4^0 is only sensitive to conduction-electron states within a region of width $\sim\pm|E_\pm|/5$ about the Fermi surface, while the comparable region for $(A_4^0\langle r^4\rangle)_{\text{cov}}$, (5.3), is $|E_\pm|$; thus even if one could determine the covalent contribution to the experimental non-S-state $A_4^0\langle r^4\rangle$, there is not necessarily a strong correlation with this value and b_4^0. It should also be recognized that even if $E_+ < |E_-|$ there can still be a relatively strong cancellation between the bonding and antibonding contributions to the non-S-state $A_4^0\langle r^4\rangle$ but no similar cancellation in (5.8) or (5.9).

To recap, the terms in b_4^0 (5.10) involving $(A_4^0\langle r^4\rangle)_{\text{cov}}$ and $(A_4^0\langle r^4\rangle)_{\text{CEC}}$ arise from different orders in perturbation theory. They therefore enter with differing coefficients and signs, and the purely covalent contribution probably dominates b_4^0.

VI. DISCUSSION

In order to judge the importance of the crystal-field processes described in the last three sections, it is necessary to estimate the size of the key parameters, the covalent mixing parameter $V_{\vec{k}f}$, and the interconfiguration energies $E_\pm$. If, as discussed at the end of Sec. V, the purely covalent contribution dominates b_4^0, then these two parameters determine $(A_4^0\langle r^4\rangle)_{\text{cov}}$, while the quotient $\zeta/E_\pm$ determines the ratio $\mathcal{R} = b_4^0/A_4^0\langle r^4\rangle$. (Note that with this division between $A_4^0\langle r^4\rangle$ and $\mathcal{R}$, the covalency parameter $V_{\vec{k}f}$ does *not* directly enter in R!)

Contributions to the covalent (or configuration) mixing parameter $V_{\vec{k}f}$ may be either intra- or interatomic. *Intra-atomic* configurational mixing has been discussed at length by Watson *et al.*[35] It should be noted that their process is identical to that which leads to the CCF, Sec. II. However, our process for $\mathcal{R}$ is *not* the CCF; the former involves the spin-orbit interaction in the intermediate rather than ground configuration. In an insulator the interconfigurational energy is very large, about 12 eV,[7] and the CCF will dominate the intra-atomic contribution. Of the two principal processes $4f^7\to 4f^6 6p$ and $4f^6 5f$, Watson *et al.* conclude $4f\to 5f$ mixing dominates. For the alloy problem we need to know the relevant $5f$ or $6p$ component of the density of states, *at the Gd site*, at the Fermi surface. The next Gd $5f$ level is high, hence its admixture must be small. The $6p$ density will be appreciable but here it is estimated[35] that the contribution is small. Fortunately, for our present purpose, this intra-atomic mixing can probably be ignored; it makes no contribution to $(A_4^0\langle r^4\rangle)_{\text{cov}}$[it therefore only contributes to b_4^0 through the term proportional to $(A_4^0\langle r^4\rangle)_{\text{CEC}}$], and following the discussion at the end of the Sec. V we expect the covalent term to dominate b_4^0. However, it may well be important to a detailed understanding of the EPR g shift.

Intra-atomic covalent mixing is a consequence of the finite amplitude to the $4f$ orbitals at the boundary of the Wigner-Sietz cell. This mixing is responsible for the finite $4f$ width in band calculations; such widths are about 0.05 eV.[25] Similar mixing leads to a d-band width of typically 5 eV. Following Heine[36] or Andersen,[37] the d-f hybridization matrix element will be about one half of the geometric mean of these two band widths; the one half corresponding to the two in a tight-binding bandwidth. This gives $V_{fd}\sim\frac{1}{2}(0.05\times 5)^{1/2}=0.25$ eV, much larger than the $V_{fd}=0.1$ eV, which leads to the estimate $(A_4^0\langle r^4\rangle)_{\mathrm{cov}}\sim 100\ \mathrm{cm}^{-1}$. This large estimate for V_{fd} corresponds to perfect bonding or antibonding with all ligands, this can only occur near the top or bottom of a band, *but might correspond to the situation, for example, near the Fermi surface in Pt or Pd, etc.* An alternative procedure is to take the Yafet[38] (see also Walstedt and Walker[39]) estimate for a d-level VBS width Δ in copper, $\Delta\simeq 0.5\ \mathrm{eV}=\pi\rho(V_{sd})^2$; this gives $V_{sd}\simeq 1$ eV. Scaling by the ratios of the roots of the band masses m_b given by Andersen[37] results in $V_{fs}\simeq 0.1$ eV, $V_{dd}\simeq 0.4$ eV and $V_{fd}\simeq 0.05$ eV. Thus our estimate, $V_{fd}\simeq 0.1$ eV, is closer to this more conservative value.

In order to discuss the size of $E_\pm$ we must briefly review the salient details of the work of Herbst *et al.*[25] These authors have investigated the factors determining the quantities $E_\pm$ in the pure rare earth metals Ce through Yb. In particular they have investigated the nature of the processes which "screen" the $4f$-$4f$ Coulomb integral usually denoted U $(=|E_+|+|E_-|)$. It has been known for a long time that this is reduced considerably from its atomic value of about 27 eV. Herbst *et al.* have shown that the experimental results for the related quantities E_- are very well explained by a "complete screening approximation." It is assumed that each Wigner-Seitz cell in the metal remains neutral when the $4f$ count is changed and that this is accomplished by changing the $5d$ count. Thus the change associated with the energy E_+ is not simply $4f^7\rightarrow 4f^8$ but rather $4f^7 5d^{1+x} 6s^{2-x}$ to $4f^8 5d^x 6s^{2-x}$. *Consequently the energies $E_\pm$ are determined principally by the relative stability of the $4f$ and $5d$ "orbitals" in the metal.* According to Herbst *et al.*,[25] the contribution to E_- which comes about from broadening the $5d$ band in a metal, etc., δE (atom $\rightarrow$ band) is about 1.8 eV for Gd metal, which represents about 20% of E_- or about one half of E_+. This contribution will vary considerably from metal to metal, depending upon the relative position and width of the $5d$ VBS or $5d$ band. In the rare earth metals this screening process is assumed to involve the $5d$-band electrons since they make the largest contribution to the density of states at the Fermi level and are therefore the most sensitive to the change in the effective potential caused by changing the $4f$ count. Similar screening can safely be assumed to occur in the hexagonal metals Sc, Y, and Lu which are isoelectronic with those considered by Herbst *et al.* and also in the metallic picnitides. In the cubic metals Au and Ag and the hexagonal metal Mg, the impurity $5d$ electrons are expected not to enter a host band but rather to form a $5d$ VBS. Consequently the $5d$ electrons will contribute the largest amount to the *local* density of states at the impurity and for this reason it is quite reasonable to expect a similar screening process to occur in these dilute alloys but now involving the $5d$ VBS. The d-band cubic metals Pt and Pd probably represent a somewhat different case. Here the top of the host d band can be expected to strongly repel the bottom of the impurity $5d$ VBS. An analogous effect can be seen in the band calculations[40] for the CsCl-structure intermetallic compound DyRh (the $4d$ band sits at the Fermi surface, an analogue of Pd). These same band calculations show that despite this, presumably because of considerable hybridization between the d bands, there is still a large density of $5d$ electrons on the rare-earth site. We suggest that the same should be true at the impurity site in Pt and Pd (implying a small $5d$ density of states at E_F). Again this charge density will be the most sensitive to the large change in potential caused by changing the $4f$ count and $5d$ screening will result. From the figure of Herbst *et al.* we obtain for pure Gd metal, $E_-=-0.6$ Ry ($\simeq 8$ eV) and $E_+=0.25$ Ry ($\simeq 3.5$ eV; the corresponding *atomic* value for Gd is ~ 1 eV), but as emphasized above these values will vary from metal to metal depending upon the relative stability of the $4f$ and $5d$ electrons.

Of the hexagonal metals Sc, Y, and Lu, only Sc can be considered as having an anomalously large ratio $\mathcal{R}$. This fits well within the above picture; both the band structures[41] and the values of $\mathcal{R}$ for Y and Lu are similar. The d band is perhaps a little higher relative to the s-p band than in Gd implying that Gd impurities in these metals will have less stable $5d$ electrons and thereby a smaller value of E_+. The d band in Sc is even higher,[41] implying an even smaller E_+. The observed value of b_2^0 corresponds to an E_+ value of 1.8 eV for Sc. Since the $5d$ band is above the Fermi surface this estimate is based upon an *s-band* contribution with parameters $V_{fs}=0.1$ eV, $\rho=0.1$ state/(eV atom spin) and $\zeta=0.21$ eV. In view of the uncertainties in the parameters, and the relative low (second) power involved, values of E_+ over quite a large range, say 1–3.5 eV, with commensurate changes in the other parameters, might fit the observed b_2^0. In these metals there is a large $5d$ density at the Fermi level and the true, positive, atomiclike, exchange J_{at} will dominate the relatively small negative covalent term in the EPR g shift. Since α is negative, the second-order parameter $\mathcal{R}$, for covalency, is *positive* and the observed negative b_4^0 corresponds to a negative $(A_4^0\langle r^4\rangle)_{cov}$, consistent with the sign of the observed non-S-state field. Again because of relatively weak dependence upon $E_\pm$ this covalent contribution to b_2^0 will be appreciable in each of these hexagonal metals and in general must be accounted for along with the insulator processes.

Of the cubic metals Pd, Pt, Au, and Ag, the two strongly enhanced metals Pd and Pt are clearly anomalous. Here corresponding to the observed b_4^0, a d-band contribution with $V_{fd}=0.1$ eV and the actual density of states, is a value of E_+ of about 1.0 eV for Pt and 1.3 eV for Pd, but again with considerable uncertainty. Both Pt:Gd and Pd:Gd exhibit large negative EPR g shifts. We suggest that in these systems the density of states at the Fermi surface, *at the Gd site*, is very small (because of a "hybridization hole") and hence the positive atomic (J_{at}), and negative intra-atomic covalent contributions are absent; the negative g shift might then be explained by interatomic covalent mixing.[42] Here for the $(A_4^0\langle r^4\rangle)_{cov}$ term $\mathcal{R}$ is *negative* and the observed, positive, b_4^0 is consistent with the experimental, negative $A_4^0\langle r^4\rangle$.

For the S-state ion Eu^{2+} values of $E_\pm \sim 1$ eV are reasonably consistent with both the calculations of Herbst *et al.*, and the observed b_4^0 in $LaAl_2$. The corresponding $E_\pm$ for Gd^{3+} will be larger than those for Eu^{2+} consistent with the absence of crystal-field effects.

VII. CONCLUSION

We have unfortunately not been able to demonstrate conclusively that the anomalously large values of $\mathcal{R}$ (or b_4^0) are associated with covalent mixing. We have shown that this is a *possible* explanation and that the conventional insulator theory fails. If our estimates, particularly of $E_\pm$, are wrong one is left with the problem stated at the end of Sec. III. Namely, to explain these large ratios $\mathcal{R}$ in metals one needs some low-lying $\Delta E \ll 4$ eV excitations which have nonzero angular momentum.

Clearly, further systematic studies of S-state and non-S-state splittings in metals would be useful; more crucial, however, is the experimental determination and/or the calculation of $E_\pm$ (and the V_{kf}) in the anomalous systems for which the crystal-field data is already known.

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