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Rare-Earth Impurities in Metals: The Configurational Transition of Ho in Liquid AgAl Solvents*

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We report measurements of the Knight shifts K and susceptibilities χ introduced by Ho impurities in liquid AlAg alloys at 1100 °C. The susceptibilities correspond to values of μ_{eff} in good accordance with those predicted by Van Vleck's theory for free ions. The value of $\Gamma = K^{-1} \partial K / \partial c$ caused by Ho impurities exhibits an abrupt transition, as a function of solvent composition, very similar to that previously observed by Blodgett and Flynn for Gd in AgAl and CuAl liquid-alloy solvents. An analysis of these data and the Ho solubility indicates that the rare earths undergo a transition in which the impurities thermally populate two available many-electron configurations that vary in relative energy with solvent composition. It appears probable that the large Γ in Al-rich solutions originate in a degenerate mixing of impurity and orbitals with host band states near E_F ; this conclusion cannot, however, be reached with complete certainty. Similar results for intermetallic compounds containing rare-earth components are also discussed.

I. INTRODUCTION

Recent studies of the magnetic properties of impurities in metals have begun to clarify our

understanding of the way in which electron-electron interactions cause particular impurity configurations to be preferred.¹ Early theoretical investigations of $3d$ -transitional impurities in simple-

metallic solvents focused attention on the one-electron $3d$ levels. A straightforward incorporation of exchange and Coulomb energies in the impurity cell leads in the Hartree-Fock theory to the Friedel-Anderson model of magnetic susceptibility and stability.^{2,3} This yields results for impurities similar to those of Stoner's model for band ferromagnetism.⁴ Later work has pointed to the additional role of configurational effects in determining impurity properties.⁵⁻⁸ Impurities are often dominated by forces similar to those in free atoms or ions and in part the metallic host lattice merely alters the relative energies of these ionic configurations. It has long been known, for example, that rare-earth ions in metals have almost precisely the magnetic properties of the spin-orbit coupled free ions, as if the host lattice had little or no effect on the coupled $4f$ electrons.⁹ For $3d$ impurities also, the spin-spin coupling in the impurity cell must far exceed in strength any coupling between individual spins and external probes. Therefore, as for rare earths, an external field merely gives preference to certain configurations without perturbing appreciably the tightly coupled impurity configurations themselves. Signs of this are clearly visible in sweeping trends of the susceptibility variation among solvents in the region of local-moment destruction.⁷ Even for nontransitional impurities it is often the over-all impurity configuration that plays the important role. Thus halides, chalcogenides, and even pnictide impurities are found to enter alkali-metal hosts as negative ions, in the 1S_0 configuration, with charge neutrality maintained by repelled band states.⁸

These diverse examples show that impurities in metals tend to adopt many-electron configurations, remarkably similar to those observed in salts, in free atoms, or in free ions. The several cases cited have configurations dominated by different aspects of the electron-electron interaction, but they have in common the fact that a local configuration with a recognizably atomic character prevails in the metallic environment. In contrast to the case of free atoms, we cannot consider impurity nuclei in metals to be neutralized by a specific set of localized electrons, for the host conduction states overlap appreciably with valence states confined in the impurity cell. The fact that the electrons forming the configuration must therefore constantly change while the atomic configuration persists provides a remarkable illustration of inter-electronic correlation in the impurity cell.

Two time intervals are important in determining impurity structure. The first of these τ_1 is the duration of one-electron collisions between host band states and the impurity; this is the period for which any single electron interacts with the impurity. In one-electron theory \hbar/τ_1 is essentially

the "bandwidth" of those one-electron levels that have large amplitudes in the impurity cell. We can obtain τ_1 from the one-electron phase shifts η , that specify the asymptotic form of the perturbed host wave functions, by¹⁰

$$\tau_1 = 2\hbar(d\eta/dE). \quad (1)$$

With one-electron bandwidths ~ 1 eV, we estimate that $\tau_1 \sim 3 \times 10^{15}$ sec is a typical one-electron lifetime for impurity orbitals in metals.

The second characteristic time τ_c measures the period for which a particular many-electron impurity configuration persists. In an isolated free atom the quantum states are infinitely long lived (neglecting spontaneous radiative decay of excited states), but even in dilute gases the energies of various configurations are lifetime broadened as collision causes transitions that establish thermal equilibrium among the various available configurations. The comparable effects of thermal perturbations for impurities in metals are augmented by a direct coupling of the impurity electrons to the thermal reservoir of the conduction-electron gas. This is both a particle source and a thermal bath; and it might therefore appear that the local density of electrons at the impurity can fluctuate wildly in time. However, since any charge excess must be screened out inside the time interval ω_p^{-1} , with ω_p the plasma frequency, it follows that the complement of electrons in the impurity cell is preserved, and that the fluctuations merely alter the configurational arrangement of the impurity electrons at a rate given by the frequency τ_c^{-1} .

A statement that correlation is important in the impurity problem simply means that $\tau_c \gg \tau_1$, so that the impurity configuration is modified only after a long series of one-electron collisions. It is easily demonstrated that this condition holds in certain cases since the observable spin resonances of magnetic ions such as Gd in Ag at low temperatures¹¹ indicate that the intact impurity moment completes many Larmor periods, occupying in all a period of $\tau > 10^{-12}$ sec. Little is known about τ_c at higher temperatures. The spin-lattice relaxation rate certainly increases but it must be noted that the dominant relaxation mechanism almost certainly (because of energy conservation) is one in which a conduction-electron spin flip merely reorients the impurity spin and leaves the relative configuration of coupled electrons intact. The relaxation time, therefore, establishes only a lower limit on the configurational lifetime τ_c , and precise measures of τ_c are entirely wanting. One result of the present work is to show that for rare-earth impurities, in liquid metal solvents at 1000 °C, the configurational width remains much less than $kT \approx 0.1$ eV, so that $\tau_c > 10^{-13}$ sec. Clear evidence for thermal repopulation among alternative con-

figurations also appears in the observed susceptibility of Sm impurities in metals.¹²

Rare-earth ions have a notable advantage over other species of impurities in metals. The $4f$ shells of free rare-earth ions provide a famous example of structures obeying Hund's rules of $\vec{L} \cdot \vec{S}$ coupling. Their magnetic properties at high temperature can be described with considerable accuracy by the equation¹³

$$\chi = \mu_{\text{eff}}^2 / 3kT + \text{high-frequency terms}, \quad (2)$$

in which high-frequency terms represent a (usually quite small) correction for components of the magnetic moment perpendicular to the resultant angular momentum $\vec{J} = \vec{L} + \vec{S}$. For our present purpose the important point is that the magnitudes of μ_{eff} predicted for the free-ion structures are in excellent agreement with the observed values. In this way the values of μ_{eff} identify particular quantum-mechanical configurations of $4f$ electrons in the free ion. The magnetic properties of rare-earth impurities in metals (and indeed, of the rare-earth metals themselves) also conform to Eq. (2) and the theoretical μ_{eff} with great fidelity.⁹ It follows, therefore, that the quantum-mechanical description of free-ion $4f$ levels must also provide an excellent first approximation to the $4f$ structure of rare-earth impurities in metals. This is in marked contrast to the more usual lack of any useful first approximation to the structure of foreign atoms in metallic hosts. It is with this point in mind that the present series of investigations were undertaken.

In this paper we report and analyze the way properties of Ho impurities depend on the host lattice of certain liquid-alloy solvent materials. Ho impurities are found to undergo an abrupt transition in AgAl solvent alloys, similar to the transition previously observed by Blodgett and Flynn¹⁴ for Gd impurities in liquid CuAl and AgAl solvents. The Gd transition was previously interpreted as taking the $4f$ impurity orbitals from bound states below the host conduction band bottom in Ag to virtual levels resonating with band states in Al. Our present rather similar results for Ho impurities are interpreted here as also marking a transition from a Ho configuration in Ag for which $4f$ levels lie below the conduction band to an alternative Ho configuration in which the $4f$ levels lie in the Al conduction band. However, while it was supposed previously that the $4f$ one-electron levels shifted continuously with solvent composition, there appears strong evidence presented here that in both the Gd and Ho cases the transition takes place directly from one configuration to the other as the configurational energies shift relative to each other with changing solvent properties. The results suggest strongly that the impurity state of lowest

energy changes with solvent composition from one to the other of two competing configurations, and the observed transition is a result of the modified thermal occupancies of the two configuration consequent upon this inversion.

It is not immediately obvious that the large changes (~ 10 eV) of $4f$ one-electron energy required for the bound-to-virtual state transition can reasonably occur in rare-earth impurities. The remainder of this Introduction concerns first this point and then finally the methods by which the transition can be detected.

Core levels in neutral atoms are highly sensitive to the precise atomic configuration. This may be demonstrated for the rare earths of interest here by reference to the Herman-Skillman¹⁵ calculations for the two alternative structures $4f^2 6s^2$ and $4f^1 5d 6s^2$ of Ce and $4f^9 6s^2$ and $4f^8 5d 6s^2$ of Tb. It is found in each case¹⁵ that *all* core levels, including the $4f$ shell, change energy by ~ 0.6 Ry (~ 8 eV) in passing from one configuration to the other. The point is that only a small change in radius of the outer valence shells is required to cause a substantial and relatively uniform change in potential over the inner core region. For example, a single valence orbital modified from 1.5 to 2 Å in radius changes the core levels by ~ 3 eV. These large changes in one-electron energy do not necessarily indicate comparable changes in the total energy of the ion. In the cases of Ce and Tb mentioned above, the competing configurations have total energies sufficiently close as to leave in doubt the question of which lies lower. The fact is, of course, that the nuclear charge also experiences the modified potential of the inner core region.

These points have particular importance for impurities in metals, because the impurity valence orbitals must necessarily suffer a considerable distortion when the impurity is incorporated into a metallic host lattice.¹⁶ In most cases, the outer shell of impurity electrons mixes into the solvent conduction band, and the sharp atomic levels are spread over a spectrum of energies with a consequent distortion of the wave functions and change in core potential. Further modifications are expected when outer d or f shells mix with the band so that ten or more orbitals may suffer appreciable distortions that contribute to the ionic potential. It is possible in certain instances¹⁷ (e.g., Ne in Na, etc.) that all impurity orbitals lie below the host band bottom so that no degenerate mixing takes place. Even so, the conduction-electron gas is scattered by the impurity potential into a self-consistent distribution that ensures the electrical neutrality of the defect cell. This screening redistribution is itself entirely analogous to a valence distortion and causes similar changes in the one-

electron impurity levels.

The electron scattering by the impurity potential also provides the mechanism employed in this work to detect the change of impurity configuration. Most rare earths have incompletely filled $4f$ levels with one spin subband more occupied than the other. For this reason the perturbation experienced by host band states is spin dependent and causes a spin-dependent conduction electron redistribution. Neighboring solvent nuclei experience a hyperfine interaction with the local unbalance of band states with opposing spin orientations, and the hyperfine field may be detected as an additional Knight shift of the solvent nuclear magnetic resonance.¹⁸

Any of several different mechanisms of spin-dependent electronic redistribution may be responsible for the Knight-shift changes, depending on the nature of the impurity. An oscillating long-range disturbance of the conduction-electron density occurs whether or not the impurity f levels mix into the conduction band. When the $4f$ levels lie below the band bottom the exchange interaction between conduction electrons and the core causes a perturbation proportional to the net core spin \vec{S} . This can be described in the limit of small coupling by the Ruderman-Kittel-Kasuya-Yoshida (RKKY) theory.¹⁹ When, on the other hand, the $4f$ levels mix into the conduction band, they cause a strong f -wave disturbance of band states degenerate with, and having the same spin orientation as, the core levels. A third alternative is obtained when "interband mixing"²⁰ causes a slight depletion of filled impurity $4f$ orbitals and a similar local accumulation of f states having the symmetry of empty impurity orbitals. Within the limitation of one-electron theory, each of these processes may be described by means of phase shifts that characterize the asymptotic form of the distorted band states. We shall turn to a discussion of these matters in Sec. III after first presenting the experimental results in Sec. II.

II. EXPERIMENTAL

The experimental studies reported in this paper continue a line of investigation begun by Stupian and Flynn,⁵ with studies of all rare earths in liquid Al, by Rigney, Blodgett, and Flynn,⁹ with studies of all rare earths in liquid Cu, and by Blodgett and Flynn,¹⁴ who studied an abrupt transition of Gd impurities in CuAl and AgAl solvents. The present report concerns the properties of Ho impurities in AgAl solutions. As in the previous studies, the quantities determined are the impurity-induced Knight-shift change, the impurity susceptibility, and, to a limited extent, the solubility of the impurity in the AgAl host lattice.

Ho was chosen for study as it is more complex ($4f^{10}$) than the case of Gd ($4f^7$) studied by Blodgett.¹⁴ It was anticipated, before our present

understanding of developed configurational effects, that the presence of electrons in both Ho $4f$ subshells might add structure to the transition from bound to virtual states. Liquid Al was chosen as a solvent possessing a readily observable nuclear resonance and known also to exhibit the unexpectedly large spin-density disturbance⁵ previously ascribed to virtual $4f$ levels. Al was diluted with Ag to obtain electron gases of various densities without greatly modifying the Al²⁷ Knight shift in the absence of Ho.

The NMR and susceptibility measurements reported here were made with equipment similar to that described by Blodgett and Flynn.¹⁴ To determine more precisely the change in Knight shift caused by Ho additions the NMR data were obtained differentially. A double probe shown in Fig. 1 was made to contain both a reference sample and the test specimen. Erratic day-to-day fluctuations of magnetic field distribution between the magnet pole faces were eliminated from the results by comparing the test sample with the reference sample *inside* the furnace assembly.

A. NMR Studies

Figure 2 shows the observed Al²⁷ Knight shift as a function of composition throughout the range of AgAl alloy compositions at 1100 °C. The rather small (<4%) shifts are in good agreement with

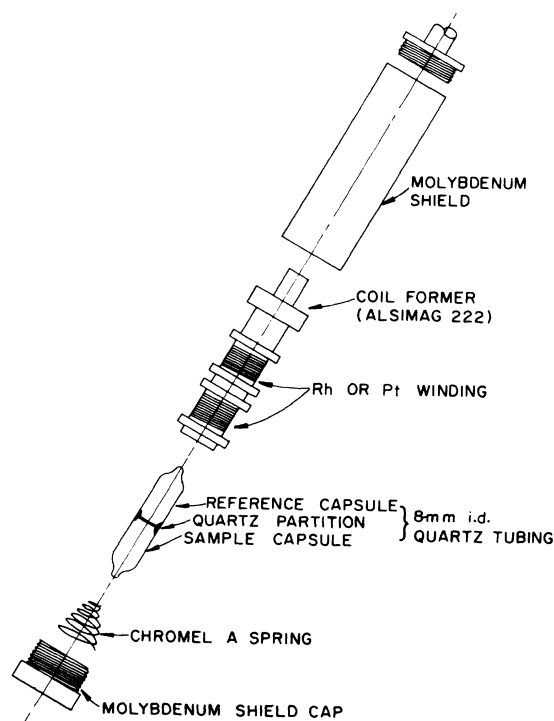


FIG. 1. Exploded view of the NMR-differential probe employed in the present work.

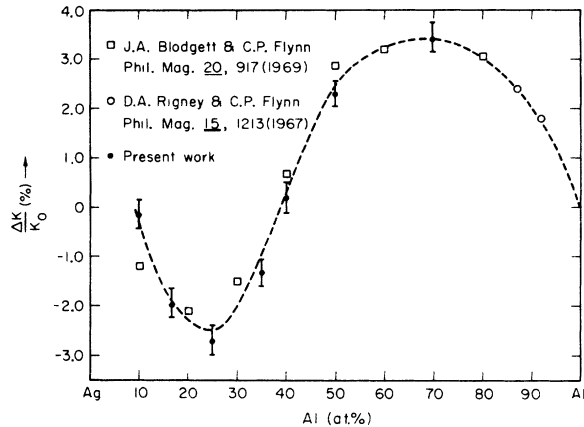


FIG. 2. Al^{27} Knight-shift change ΔK as a function of composition in liquid-AgAl alloys at 1100°C .

previous less precise results,¹⁴ residual systematic differences being much too small to affect the conclusions drawn from the earlier studies. Thus, by virtue of the small, reproducible shifts, AlAg proves to be a suitable host lattice for Knight-shift studies.

Ho additions to liquid AlAg solvents at 1100°C caused the added shifts indicated by the values of $\Gamma = K_0^{-1}(\partial K/\partial c)$ in Fig. 3. Here, K_0 is the pure Al Knight shift and K that in the alloy solvent, with c the concentration (atomic fraction) of Ho impurity. Previous detailed studies have revealed that K is linear in c for $c \leq 0.05$ in these liquid materials,^{5,9,14} although the skin effect can introduce large non-linear effects under less favored circumstances.²¹ The observed Γ agree well with the previous result for Ho in pure Al.⁵ At host compositions neighboring $c_0 \sim 37$ at.% Al, 63 at.% Ag, Γ is observed to fall abruptly from ~ -8 to ~ -1 , as found by Blodgett and Flynn¹⁴ for Gd in CuAl and in AgAl. It should

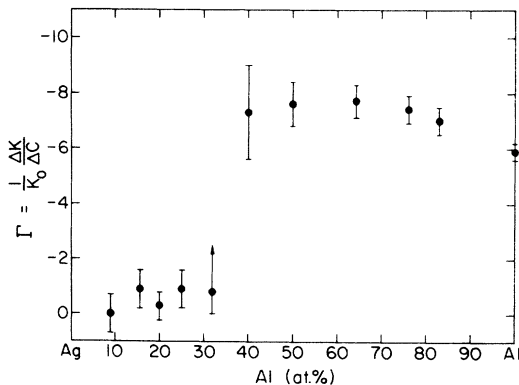


FIG. 3. Additional Knight-shift changes ΔK caused by Ho impurities in liquid-AgAl alloys at 1100°C . The changes are given in terms of $\Gamma = \Delta K/cK_0$ with c the Ho concentration and K_0 the Knight shift in pure Al.

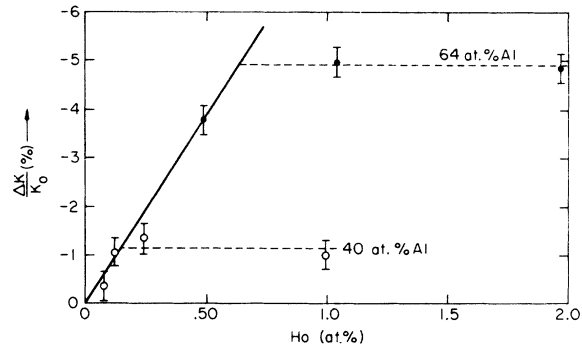


FIG. 4. Knight shift as a function of Ho impurity concentration in two AgAl solvent alloys at 1100°C . The sharp break indicates the limiting solubility in each case.

be remarked that the spin-dependent Γ in Cu (and hence probably also in Ag) is ~ 0.1 ,⁹ and that the coupling between the nuclear spins and the $4f$ core levels therefore decreases by about two orders of magnitude. As far as can be judged, the Ho and Gd transitions occur over similarly small ranges of solvent electron density.

Any attempt to determine accurately the width and shape of the transition is discouraged by a remarkable decrease in Ho solubility near the transition. Figure 4 shows how the Al^{27} Knight shift saturates with Ho concentration c for $c \approx 0.1$ at.% when the solvent contains $c_0 = 40$ at.% Al and at $c \approx 0.6$ at.% when $c_0 = 64$ at.% Al. We presume that the nonlinearities signal the limiting Ho solubilities in those hosts. The maximum solubility deduced in this way for Ho in various AgAl solvents, shown as a function of host composition c_0 in Fig. 5, exhibits a marked minimum at the transition. Similar effects were found for Gd impurities in CuAl.¹⁴ The unfortunate fact that Ho proves less soluble than Gd has limited the accuracy available in the present studies of the interesting transition region.

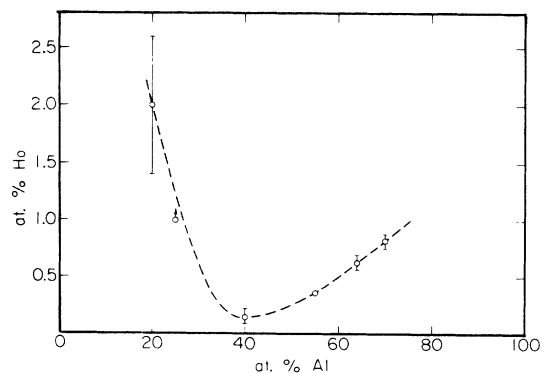


FIG. 5. Maximum solubility c of Ho in AgAl alloys at 1100°C .

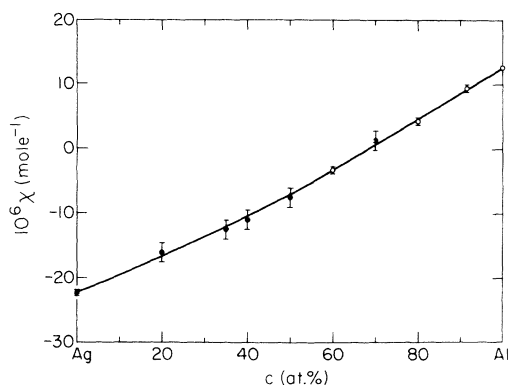


FIG. 6. Susceptibilities of AgAl liquid alloys at 1100 °C.

B. Susceptibility Studies

As mentioned above, the susceptibility of rare-earth ions provides an accurate monitor of their $4f$ configuration. The Ho susceptibility was therefore determined through a range of host compositions spanning the transition. Figure 6 shows how the susceptibilities of the liquid AgAl solvent alloys vary smoothly with composition across the entire range of the phase diagram. Figure 7 shows the additional susceptibilities introduced by Ho impurities in these alloys, expressed as values of μ_{eff} . The observed value agrees with the theoretical $\mu_{\text{eff}} = 10.6 \mu_B$ to within the experimental uncertainty. It seems in particular for Al-rich alloys that μ_{eff} does not deviate by more than $\pm 0.3 \mu_B$ from the theoretical value. This result plays an important part in our subsequent interpretation. Furthermore, although the uncertainties are largest near the transition because of solubility problems, there appears no reason to believe that μ_{eff} is modified significantly by the transition.

III. DISCUSSION

A. Significance of Susceptibility Results

We shall discuss impurity structure within the one-electron approximation and for an isotropic host lattice. The phase shifts induced by the impurity potential into the conduction-electron partial waves then serve to specify both the impurity structure and the wave functions outside the impurity potential. An impurity causing energy-dependent phase shifts $\eta_{lms}(E)$ for electrons of spin s and angular momentum l having a projection m on the quantization axis has a density of impurity states¹⁶

$$N_{lms}(E) = \left(\frac{1}{\pi} \right) \left(\frac{d\eta_{lms}}{dE} \right) \quad (3)$$

with those quantum numbers. In this way the phase shifts as functions of energy specify the impurity

structure within the Hartree-Fock approximation to a degree comparable with a tabulation of the energy and symmetry of the occupied bound orbitals in insulators. Supplementary information concerning orbitals bound below the band bottom is also required for the case of impurities in metals.

It is worth emphasizing here that the phase shifts provide a general one-electron description and that alternative perturbative treatments employed to describe impurity effects are merely particular approximations to the general phase-shift results. We shall comment further on the RKKY approximation after an important point concerning the susceptibility is established.

From Eq. (2) we find that the occupation of an orbital with the phase shift $\eta_{lms}(E)$ is

$$n_{lms} = \int_0^{E_F} N_{lms}(E) dE = \frac{1}{\pi} \eta_{lms}(E_F). \quad (4)$$

A completely full orbital with $n=1$ evidently has $\eta(E_F) = \pi$, whereas a completely empty orbital has $n=0$, and therefore $\eta(E_F) = 0$. Since we may clearly suppose that truly bound orbitals below the band are fully occupied, it follows that the occupation of any angular-momentum state differs from 0 or 1 only to the extent that $\eta(E_F)$ differs from 0 or π . Now the μ_{eff} for Ho impurities in metals agrees with theory for free ions to within $\pm 0.3 \mu_B$ in $10.6 \mu_B$, or to about $\pm 3\%$. It follows from Eq. (5) that the orbitals in the metal are fully occupied or fully empty to this precision, so that

$$\eta_{3ms} = 0(\text{mod } \pi) \pm 0.1 \text{ rad} \quad (5)$$

holds for Ho impurities. Similar conclusions may be reached for most other rare earths from the available data.

Note that the observed susceptibilities also rule out the possibility that valence orbitals exhibit either a spin or an orbital magnetization along μ_{eff} of magnitude greater than $\sim 3\%$ of μ_{eff} (neglecting

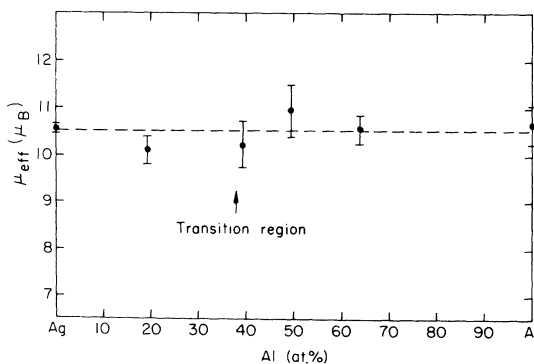


FIG. 7. Observed effective magnetic moment μ_{eff} that describes the susceptibility of Ho impurities in AgAl solvent alloys at 1100 °C.

the possible fortuitous cancellation of several additive contributions to μ_{eff}). This conclusion holds for rare earths dissolved in liquid Al,⁵ Cu,⁹ and Ag¹⁴ but not for rare earths in solid Sc where μ_{eff} is substantially increased and made anisotropic by the noncubic environment.²²

B. Significance of Observed Knight Shifts

The large Knight-shift changes caused by rare-earth impurities in simple metals arise from a coupling between the core spin \vec{S} and the host band electrons. This conclusion follows from the fact that Γ varies with T and with impurity species in a way unmistakably associated with the field-induced $4f$ spin polarization

$$\langle S \rangle \sim g(g-1) J(J+1) \mu_B H / 3kT. \quad (6)$$

Thus, the origin of the shifts appears to be beyond question. What seems to remain in doubt is the mechanism by which the $4f$ cores couple to the conduction band. We shall show in what follows that the RKKY mechanism can never adequately describe the size and sign of the observed Γ . Both the degenerate mixing of $4f$ levels into the band near E_F and the "interband mixing" mechanisms can possibly produce the correct size and sign of Γ . In the case of interband mixing, however, only an optimal choice of parameters can make the predicted shifts approach the large size of the observed Γ , and then the possibility remains only marginal.

1. RKKY Exchange Mechanism

It has been noted elsewhere that the RKKY interaction is likely to have quantitative success only for the weak interactions between host nuclear spins^{19,23,14}; this is the case for which it was first derived. The RKKY interaction in its customary form appears only as the limit of weak spin-dependent s -wave scattering. When the valence s -wave scattering is also weak enough to be described by the Born approximation, an impurity causes a spin-density disturbance¹⁴

$$\delta n(x) = \frac{3n}{8} \left(\frac{\sin 2(x + \eta_-)}{x^2(x + \eta_-)} - \frac{\sin 2(x + \eta_+)}{x^2(x + \eta_+)} \right), \quad (7)$$

with $x = k_F r$. Here $n = k_F^3 / 3\pi^2$ is the host electron density and η_+ and η_- are the s -wave phase shifts at the Fermi energy for electrons with spin up and spin down, respectively.

Γ can be calculated for this mechanism by comparing the spin polarization caused by oriented impurities, according to Eq. (7), with the spin polarization caused by solvent Pauli paramagnetism in an applied field. The result is

$$\Gamma = \frac{4 E_F g(g-1) J(J+1)}{9kTS} \int_0^\infty f(r) \delta n(r) r^2 dr$$

$$\sim 1.2 \times 10^3 \int_0^\infty k_F^{-3} f(x) \delta n(x) x^2 dx \quad (8)$$

for Gd with $J = S = \frac{7}{2}$, $g = 2$, and for $E_F/kT \approx 100$ as is appropriate in the case of Al at 1000 °C. In Eq. (8), $f(r)$ determines the probability $P(r) dr$ of finding a solvent nucleus at r from the impurity according to the relation

$$P(r) = 4\pi f(r) r^2 / \Omega, \quad (9)$$

with Ω the solvent atomic volume. Thus $f(r) \approx 0$ out to the first-neighbor sites and $f(r) \approx 1$ thereafter. The first neighbors lie at $x \sim 5$ for trivalent metals so that each term contributed by $\delta n(x)$ to the dimensionless integrand in Eq. (8) is $\lesssim 2 \times 10^{-3}$. As each term oscillates with period π as x increases, we see that the RKKY interaction cannot contribute the observed $|\Gamma| \sim 10$ *however large the coupling to the band may be*. The point is that the spin-density disturbance depends only on $\eta(\text{mod } \pi)$ and does not increase without bounds.

In the present case we are further restricted by the susceptibility data to set $|\eta_+ - \eta_-| < 0.1$ rad. The two terms in Eq. (7) then largely cancel and the RKKY Γ becomes of no significance. Note that it matters little that the RKKY interaction in trivalent hosts has the wrong sign. The sign merely alters the phase of the density oscillation which is, in any event, perturbed by valence effects¹⁴ for impurities, as indicated by Eq. (7). The main point is that the RKKY interaction can never approach the order of magnitude of the observed effects in Al-rich alloys. There is no reason to suppose that exchange scattering of higher partial waves can change this conclusion to any significant extent.

2. Degenerate Mixing Mechanism

Degenerate mixing occurs when $4f$ core levels resonate with band states near some energy E_{4f} . The f -wave phase shift rises from 0 to π near E_{4f} for the occupied f orbitals, while the phase shift must remain near zero for the unoccupied orbitals. From the observed μ_{eff} it follows that the phase shifts at E_F are within ± 0.1 of $0(\text{mod } \pi)$.

The host band states are perturbed whenever $\eta \neq 0(\text{mod } \pi)$. In the present case the occupation of orbitals is spin dependent and a spin-density redistribution occurs. The contribution to Γ per $4f$ orbital is found to be⁵

$$I = \int_0^{k_F} k^2 [A_3(k) \sin^2 \eta_3(k) + B_3(k) \sin 2\eta_3(k)] dk, \quad (10)$$

with A and B functions that can be calculated from $f(r)$. When η rises from 0 to π over a narrow range κ of k near k_F , one finds the following narrow band result for degenerate mixing:

$$I_{dn} \approx A(k_F) k_F^2 \int_0^{k_F} \sin^2 \eta dk. \quad (11)$$

Here it is assumed that the band shape specified by $d\eta/dE$ is symmetrical so that the term in $\sin 2\eta$ vanishes. $A(k_F) \sim -2.5$ for trivalent materials. Using this and the observed Γ , Stupian and Flynn⁵ deduce that

$$\int_0^{k_F} \sin^2 \eta(k) dk = 1.3 \times 10^{-2} k_F \quad (12)$$

for rare earths in liquid Al. This corresponds to a full $4f$ bandwidth of ~ 0.5 eV.

Thus, the observed Γ follow very easily from the theory for degenerate mixing. Only narrow f bands are required to cause the observed shifts, and the observed sign follows whenever the $4f$ states fall within $0.2k_F$ of the Fermi surface.⁵ It should be reemphasized that the spin-density distribution causing the shift does not in this case have the traditional oscillatory form decaying as r^{-3} with distance from the impurity. Rather, the spin polarization is concentrated in a sphere of radius $\sim (\kappa)^{-1}$ around the impurity. The reason is that long-range effects of the form r^{-3} are caused by perturbed states at the Fermi limit k_F . In the present case the phase shifts are $0(\text{mod } \pi) \pm 0.1$, so the states at k_F are little perturbed. Instead, the polarization arises from states near E_{4f} and the disturbance takes the approximate form

$$\delta n(r) \sim r^{-2} e^{-\kappa r} \cos(2\kappa r + \phi), \quad (13)$$

with k the wave vector at E_{4f} and ϕ some mean phase angle.

3. Interband Mixing

As noted above, all coupling mechanisms between the host conduction band and an impurity potential are described in Hartree-Fock theory by the phase shifts as functions of energy. Watson *et al.*²⁰ have pointed to an interband mixing effect that causes an emission of f electrons from occupied f orbitals at the impurity into the conduction band near E_F , and an analogous absorption of electrons into unoccupied impurity f orbitals. The effect was discussed first for intermetallic compounds containing rare-earth components,²⁰ but there appears no reason why similar processes should not occur at localized impurities in foreign host lattices. Watson *et al.*²⁰ note that two processes, one involving local p -like band states and the other f -like band states, contribute to the interband mixing effect. The calculations are apparently difficult to conduct from first principles and there appears at present to be no reliable guide to the magnitude of their effect on Γ .

Fortunately, we can discount on experimental

grounds any profound influence of p -like band states on Γ . It has previously been shown^{5,14} that Eu ($4f^7 6s^2$) and Gd ($4f^7 6s^2 6p$) give similar values of Γ despite a valence change that must surely modify significantly the density of p -like band states that overlap in space with the half-filled $4f$ shell (the band states are, of course, the rare-earth valence orbitals inside the impurity cell). It seems safe, therefore, to ignore band states of p symmetry and to focus attention on processes involving f -like band states and f -like core states alone. These processes are extremely simple; they consist merely of a partial transfer of f -symmetry orbitals from local to band states, and are described in Hartree-Fock theory by the f -wave phase shift as a function of energy. In effect, the interband mixing acts as a local isotropic potential that may influence the variation of η_3 with E . The emission processes studied by Watson *et al.* correspond for full orbitals to a reduction of the localized f -wave density with increasing energy and hence to a decrease of $\eta_3(E)$ below the value π for $n=1$. Similarly, absorption increases $\eta_3(E)$ for empty orbitals above the value 0 for $n=0$. The result, as previously remarked by Blandin,²⁴ is the pattern of f -wave phase shifts shown for bound and virtual $4f$ levels in Fig. 8. There is nothing unusual about the phase shifts in Fig. 8; they are qualitatively identical with the behavior expected for one-particle scattering from an isotropic well giving rise, in the two cases, to sharp spin-dependent bound or virtual levels.

We shall for this discussion indicate by "degenerate mixing" the sweep of phase shifts from 0 to π through the energy region in which an occupied core orbital hybridizes into the conduction band. By interband mixing we shall signify any reduction of η below π above E_{4f} or any increase of η above 0 for an empty orbital. It is our opinion that these latter features of the density of impurity states may arise from a variety of distinct causes related to features of the impurity potential, and that the notion of interband mixing may itself only be useful in the absence of hybridization (degenerate mixing) when the $4f$ levels are bound. Nevertheless, the name interband mixing will serve here to specify a particular aspect of impurity structure that may contribute significantly to Γ .

It is easy to calculate approximately the largest possible effect of interband mixing on Γ . Suppose that the phase shift η_f for a filled bound f orbital takes the form

$$\eta_f = \pi - \eta(k_F) k^7 / k_F^7 \quad (14)$$

and that for an empty orbital

$$\eta_e = \eta(k_F) k^7 / k_F^7. \quad (15)$$

In these expressions $\eta(k_F)$ is the deviation of η

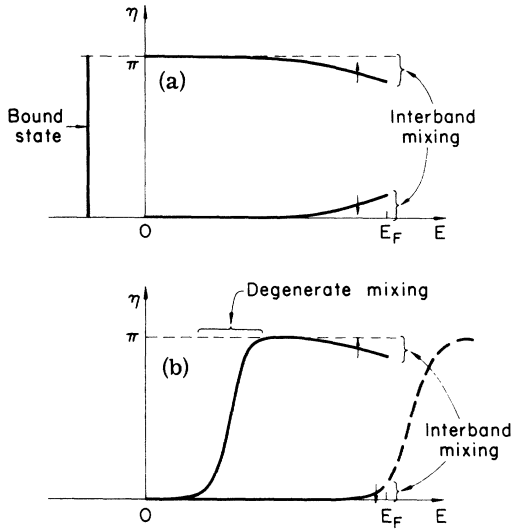


FIG. 8. Patterns of f -wave phase shift for (a) bound states and (b) virtual states. The features described as degenerate mixing and interband mixing are indicated.

from $0(\text{mod } \pi)$ at the Fermi limit, and this deviation is presumed to emerge at k^7 with increasing k , in accordance with the Born approximation to potential scattering.¹⁰ Using Eq. (10), the effect of an occupied orbital on Γ may now be expressed for $\eta(k_F)$ small in terms of an integral

$$I_{1m} \simeq - \int_0^{k_F} B(k) \sin[2\eta(k_F)k^7/k_F^7]k^2 dk \simeq -\frac{1}{5}k_F^3 B(k_F) \eta(k_F), \quad (16)$$

in which the integral is evaluated for $\eta(k_F)$ small and $B(k)$ slowly varying near k_F .

Each occupied and unoccupied orbital contributes an integral to Γ of the magnitude given by Eq. (16). At the same time each occupied and unoccupied orbital contributes to a deviation of the magnetic moment from the ionic value. As occupied and unoccupied orbitals contribute equally the observed susceptibilities limit $\eta(k_F)$ to a value less than 0.05 rad. Using Eq. (11) to obtain the observed value of the integral I we can now express the ratio of Γ_{1m} , the maximum Γ possible from interband mixing, to the observed Γ_{obs} as

$$\frac{\Gamma_{1m}}{\Gamma_{\text{obs}}} = - \frac{\frac{2}{5}k_F^3 B(k_F) \eta(k_F)}{k_F^2 A(k_F) \times 1.3 \times 10^{-2} k_F} \leq 0.3 \quad (17)$$

for the values $A(k_F) = -2.5$, $B(k_F) = 0.5$, and $\eta(k_F) \leq 0.05$. Thus, the observed susceptibility is so close to the free-ion susceptibility that deviations of the phase shifts from $0(\text{mod } \pi)$ are too small to cause the observed Γ .

Unfortunately, this conclusion cannot be held in full confidence because the values of $A(k_F)$ and $B(k_F)$ are not known with accuracy and because the

estimated $B(k)$ increases with decreasing k in a way that could bring the maximum possible Γ_{1m} into the range of the observed Γ . Substantially more precise susceptibility data for these dilute impurities would be required to eliminate entirely the possibility that Γ contains substantial contributions from interband mixing.

In summary, then, we note that the values of μ_{eff} and χ for rare-earth impurities in metals do not point unequivocally to any particular impurity structure. The observation found comfortable explanation in size and sign from the degenerate mixing of $4f$ orbitals into the conduction band between $0.8k_F$ and k_F , with a bandwidth $\sim 10^{-2}k_F$, as proposed by Stupian and Flynn.⁵ On the other hand, it is not possible with the existing data on Γ and χ to exclude the possibility that the $4f$ levels remain either below the band bottom, or low in the band, and that the observed Γ originate in small deviations of the phase shifts from $0(\text{mod } \pi)$ over broader regions of k space. This latter mechanism, indicated in Fig. 7(a), may well be too weak but cannot at present be entirely discounted. Further insight into the impurity structure is obtained from the Γ transition itself, and it is to a discussion of this transition that we now turn.

C. Transition from Large to Small Γ

We have seen that the coupling between impurity core spins and host nuclei is reduced abruptly in solvents containing 63 at. % or more Ag. The relevant experimental facts may be summarized as follows:

(a) The strong coupling observed in pure Al is further increased by $\sim 25\%$ in passing to alloys containing 60 at. % Ag. A similar increase is observed for Gd impurities.¹⁴

(b) The spin-dependent coupling in pure Cu was previously found to be two orders of magnitude smaller than in Al. In conjunction with previous Gd data for AlAg solvents, the present Ho results indicate that the coupling in alloys containing 25 at. % Al remains at least one order of magnitude smaller than that in 40 at. % Al alloys. Therefore the transition is sharp in the sense that Γ varies one to two orders of magnitude faster with Al concentration in the transition region than outside the transition region.

(c) Earlier studies show that Eu ($4f^7$) and Gd ($4f^7$) give similar Γ in Al despite the change of valence from 2 in Eu to 3 in Gd.

Whether the large Γ in Al arises from degenerate or interband mixing it is necessary to explain how an abrupt transition in coupling strength can occur. This transition is unlikely to involve a valence rearrangement, in view of point (c) above, and certainly causes no appreciable change of susceptibility or $4f$ core structure. Given these stringent restric-

tions we have been unable to hypothesize any origin for the transition other than that type in which the core and valence levels shift into degeneracy and so couple together more strongly. This being the case the strong coupling mechanism occurs either when the f levels lie high in the conduction band and couple to the band by hybridization or when the f levels lie lower in the band and the coupling to impurity nuclei takes place because the phase shifts at higher energies deviate from $0(\text{mod}\pi)$. In either case the weak coupling observed in monovalent solvents probably does arise from an exchange coupling between band states and truly bound $4f$ orbitals. As remarked in Sec. IIIB, the degenerate mixing mechanism of strong coupling appears the more likely but cannot be identified with certainty.

In analyzing the transition itself we must acknowledge two distinct processes by which an impurity may change from one structure to another. First, we may imagine that the impurity one-electron levels distort smoothly with changing solvent characteristics until the impurity eventually passes from one structure (say, in Ag) to a second (in Al). Second, as mentioned in the Introduction, it is possible that an impurity can exist in a number of distinct configurations having differing total energies that change smoothly with solvent structure. We shall refer to the first type of transition as a one-electron transition and to the second as a configurational transition. Neither transition has been studied experimentally or subject to extensive theoretical discussion, although Mott²⁵ has remarked on the limited lifetimes of one-electron levels close to the band bottom, and Kohn and Majumdar²⁶ have examined the one-electron transition for a gas on noninteracting particles. More recently, Flynn and Lipari¹⁷ have investigated quantitatively the way in which higher valence impurities bind states in alkali metal hosts, but by methods that break down in the limit of weak binding. Consequently, there is available at present neither theoretical nor experimental guidance as to the behavior expected in either configurational or one-electron transitions.

There seems, nevertheless, to be an experimental distinction that can be drawn between these two types of transitions. A transition that arises from a continuous variation of one-electron levels need not be abrupt, for the coupling must vary progressively as the changing solvent properties gradually alter the one-electron levels. In the case of a transition to virtual levels high in the conduction band one might expect structure on the transition because the virtual levels probe the band at different energies for different host alloys. An added structure might appear in the present case of Ho impurities from the fact that the two Ho $4f$ -spin subbands lie at different energies.

Finally, it is not clear that the smoothly changing one-electron levels could possibly give rise to abrupt changes in thermodynamic properties at the Γ transition.

Each of these points appears to be modified for a configurational transition. A change from one configuration to the alternative state must take place abruptly as the configurational energies cross. Moreover, since the transition takes place from one stable configuration to another, the observed Γ should be rather stable outside a narrow region in which the alternative configurations are essentially degenerate in ways discussed below. Features of the one-electron levels cannot add structure to the configurational transition. Finally, since the transition takes the impurities to an entirely new configuration, there may be substantial changes of thermodynamic properties.

It is clear that the observed sharp structureless Γ transition between values that are stable over wide ranges of host composition fits far better the case of a configurational transition than the one-electron alternative. Furthermore, the observed solubility dip provides direct evidence of thermodynamic changes that support this choice. In the remaining discussion we analyze in somewhat more detail both theoretical and experimental aspects of the transition.

Figure 9(a) shows the energies $E_c(c_0)$ and $E_b(c_0)$ of two configurations a and b varying smoothly and in different degrees as the host-alloy concentration c_0 is changed. The two energies remain degenerate within the thermal energy of kT for a range of solvent compositions that determines the width of the transition, as indicated in Fig. 9(a). The transition can be broadened further by the limited configurational lifetimes τ_c as shown in Fig. 9(b), or by an interaction between the configurations caused by the lattice potential [see Fig. 9(c)].

We may anticipate that the maximum Ho solubility c in an arbitrary solvent of concentration c_0 follows approximately an equation of the form

$$c(c_0) = Ae^{-E(c_0)/kT}, \quad (18)$$

in which $E(c_0)$ is a heat of solution and A is an entropy factor.²⁷ Thus, for configuration a stable in Ag-rich alloys one has

$$\ln c_a(c_0) = \ln A_a - E_a(c_0)/kT, \quad (19)$$

and similarly for configuration b stable in Al-rich alloys we have

$$\ln c_b(c_0) = \ln A_b - E_b(c_0)/kT, \quad (20)$$

in which subscripts identify the parameters with one particular configuration. In what follows we neglect for convenience the possibility that A_a and A_b vary with c_0 , on the grounds that the major variations of c are likely to rise from changes in E with c_0 .

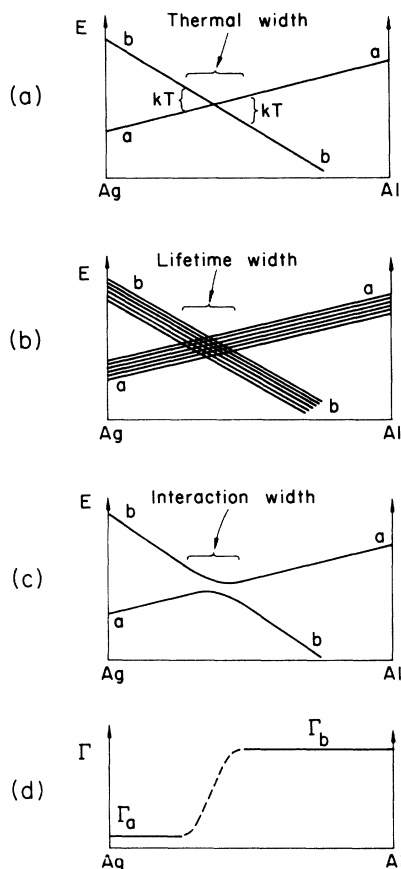


FIG. 9. Various broadening mechanisms for a configurational transition. (a) Broadening by thermal repopulation; (b) broadening by limited configurational lifetimes that give the configurational levels a nonzero width; (c) broadening by configuration interaction; (d) the resulting Γ transition.

Figure 10 shows the observed maximum Ho solubilities plotted as $\ln c$ against the solvent composition c_0 for a temperature of 1100 °C. The figure includes the 100% solubility of rare earths in pure Cu at this temperature, and the solubility ~10% of rare earths in Al.²⁸ The data on either side of the transition are compatible with a smooth variation of $\ln c$ with c_0 as if the entropy factors were indeed sensibly constant and the energies varied rather linearly with c_0 . With a thermal energy $kT \sim 0.12$ eV at these temperatures the extrapolations shown in the figure indicate that configuration *a* (bound orbitals) increases in energy by 2.2 eV in passing from pure Ag to pure Al. Configuration *b* (virtual levels) is found to decrease in energy by 0.8 eV in passing from pure Ag to pure Al. It should be stressed that Fig. 10 bears a remarkable similarity to any of Figs. 9 [9(a)–9(c)] and that the energy changes of 0.8 and 2.2 eV have precisely

the order of magnitude expected for energies of solution and their changes from one solvent to the next. Furthermore, the intersection of the two experimental lines occurs precisely at the Γ transition, as expected for the configurational transition. These points appear to add overwhelming evidence in favor of the configurational nature of the transition. The previous less precise solubility results for Gd in CuAl contribute to a similar conclusion.¹⁴

There is a final point that allows us to distinguish among the configurational broadening mechanisms depicted in Fig. 8. The hatched portion of Fig. 10 indicates the spread of the Gd transitions in AgAl and CuAl and of the Ho transition in AgAl. It will be apparent from the figure that the observed width encompasses precisely that range of solvent in which the two configurations have equal occupancies within a factor of 3 or so. Thus, essentially the entire broadening originates in the thermal repopulation process. It follows that configuration interactions are limited to splittings of at most a few hundredths of an electron volt. A similar limitation on the configurational width indicates the more important consequence that the configurational lifetime must exceed 10^{-13} sec.

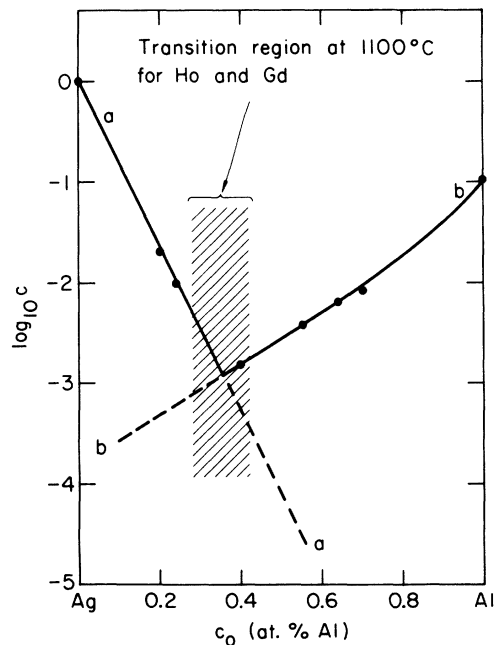


FIG. 10. Logarithm of the observed maximum solubility of Ho in liquid AlAg at 1100 °C indicates the energies of two competing configurations as a function of host-alloy composition. The hatched region shows the maximum range of the observed Γ transition of Gd in CuAl and of Ho in AgAl. It appears to occupy the range of thermal repopulation between the competing configurations.

D. Analogous Results for Compounds

Large temperature-dependent Knight shifts have been observed in intermetallic compounds containing the rare-earth ions as one component.²⁹ The shifts have been found to vary from one rare earth to the next in approximate proportion to the core spin polarization $\langle S \rangle$. This similarity between the results for impurities and for compounds is broader than appears immediately evident and we believe that the two sets of results must originate in a common cause. For example, in HoAl_3 compounds at 100 °K, the Al^{27} Knight shift is observed to be $\Delta K = -4\%$.³⁰ Using $K = 0.16\%$ for Al and $c = 0.25$ as the Ho concentration, one thus finds

$$T\Gamma = T\Delta K/Kc = -10^4 \text{ }^\circ\text{K},$$

which compares very favorably with the value $\Gamma \simeq -8$ at $T \simeq 1273 \text{ }^\circ\text{K}$ observed in our investigations of dilute Al-based alloys.

Even more remarkable is the fact that a transition has been observed to take place in compounds containing rare earths. It is a transition in which the exchange constant required to explain K using RKKY theory changes sign to become unphysically negative.²⁹ The results are less easy to decipher as the band structures of these compounds are poorly understood. It nevertheless seems that the transition takes place rather abruptly with increasing electron density in the compound, and hence with increasing k_F . The similarity with our own results is made rather complete by the fact that negative "exchange constants" are observed only in compounds containing large proportions of Al. As

noted above, our results for dilute Al based alloys are much too big, and also have the incorrect sign for an explanation involving RKKY theory to account for the observed Knight shifts.

It is not, perhaps, too surprising that the shifts observed in regular compounds and in dilute liquid alloys are so similar. The linearity with c of the observed K in liquid alloys makes it very likely that for rare-earth concentrations of $c = 0.25$ in the liquid (at 1500 °C) one would observe almost precisely the ΔK observed in the solid compound obtained by cooling the liquid alloy. What these results tell us, then, is that Γ is insensitive to the geometrical structure of the host lattice. For this reason it seems unlikely that precisely evaluated RKKY-like sums of hyperfine interactions, over many shells of neighbors to the rare-earth ion, play any critical part in determining Γ .

IV. SUMMARY

Rare-earth impurities undergo an abrupt transition from a configuration that interacts weakly with the host band in Ag-rich liquid alloys to a configuration that interacts strongly with the host band in Al-rich alloys. Similar effects are observed in solid compounds. It seems most likely that the rare-earth $4f$ levels resonate with band states near E_F in Al-rich materials and lie at much lower energies probably below the band in lower valence materials. However, the possibility that the f levels lie lower in the band for Al-rich solvents and disturb the band through deviations of η_3 from $0 \pmod{\pi}$ cannot at present be eliminated with certainty.

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PHYSICAL REVIEW B

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Theory of the Magnetic Susceptibility of Bloch Electrons*

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It has heretofore always been assumed that the magnetic susceptibility of a crystal could be written $\chi = \chi_{\text{dia}}^{\text{core}} + \chi_{\text{dia}}^{\text{val}} + \chi_{\text{spin}}^{\text{val}}$, where $\chi_{\text{dia}}^{\text{core}}$ is the contribution of the core electrons, $\chi_{\text{dia}}^{\text{val}}$ is the contribution of the orbital motion of Bloch valence or conduction electrons completely neglecting spin, and $\chi_{\text{spin}}^{\text{val}}$ is the Pauli spin paramagnetism but with the free-electron g factor replaced by the effective g factor. The entire effect of spin-orbit coupling is assumed to be included in the effective g factor. We show that this is not the case and that there is a large fourth contribution to χ , the effect of the spin-orbit coupling on the orbital motion of the Bloch electrons χ_{so} . We construct a many-band Hamiltonian using the Bloch representation and derive the susceptibility directly from this Hamiltonian avoiding the ambiguity of the usual decoupling transformations. Our result agrees with the expression derived by Roth but is in a much more transparent form.

I. INTRODUCTION

The pioneering work on the quantum theory of diamagnetic susceptibility of free electrons was done by Landau¹ who showed that for a degenerate electron gas the diamagnetic susceptibility per unit volume is

$$\chi_L = -e^2 k_0 / 12\pi^2 mc^2, \quad (1.1)$$

where k_0 is the wave number at the top of the Fermi surface. The expression for the spin susceptibility of free electrons obtained by Pauli² is three times larger than Landau diamagnetism and is of opposite sign. Therefore, a degenerate electron gas is always paramagnetic. However, the periodic potential in a solid changes the magnitudes of the diamagnetic and paramagnetic effects and also causes a coupling of the two effects through spin-orbit interaction.

The first step in understanding the diamagnetism of Bloch electrons was made by Peierls.³ He constructed an effective Hamiltonian using wave functions obtained in a tight-binding approximation and obtained three terms for the magnetic susceptibility, the leading term of which reduces to the Landau formula in the case of free electrons and is called the Landau-Peierls susceptibility. How-

ever, in this theory, both the interband effect and the many-body effect had been ignored. Further, the tight-binding approximation is not valid for many solids.

Adams⁴ stressed the importance of the interband terms in the effective Hamiltonian when the energy gaps are small. He gave a general treatment of the interband effect and then examined a simple example of two bands separated by a small energy gap produced by the Bragg reflection of a weak one-dimensional cosine potential. He considered two particular cases. The first is the case where the number of electrons in the upper band is small and so all of these electrons are influenced by Bragg reflection. The second case is that where the upper band contains a large number of electrons and so only a smaller fraction of the electrons are affected by the periodic potential. However, Adams's expression for the second case has the defect that in the limit of a vanishing periodic potential it gives a divergent result.

Wilson⁵ obtained the density matrix directly as a power series in the magnetic field in terms of the solutions of the Schrödinger equation when the field is zero. The calculation of the susceptibility then becomes a computational problem, but in practice the computation becomes so intractable