Fundamental Parameters and Mechanisms in the Ce Problem: Photoemission Results on CeAl₂ and CeAl₂ Alloys

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Photoelectron-spectroscopy studies of $CeAl_2$, $LaAl_2$, and the "chemically compressed" alloys $Ce_{0.6}Y_{0.4}Al_2$ and $Ce_{0.6}Sc_{0.4}Al_2$ were performed with use of synchrotron radiation. For all compounds the $4f$ binding energy is 2.55 ± 0.1 eV. These results, combined with previous bulk-property results, motivate a reevaluation of Anderson-model parameters and mechanisms as applied to $CeAl_2$.

Elemental Ce has two fcc phases, the high-volume, local–magnetic-moment γ phase and the low-volume, Pauli-paramagnetic α phase.[1] In general, the effective volume and magnetic character of Ce in intermetallic compounds can be characterized as being γ-Ce–like or α-Ce–like.[2] Indeed, this partitioning of Ce systems (at least in terms of magnetic properties) can be extended to numerous dilute Ce systems.[2,3]

Over a number of years a large body of theoretical work, rooted in the Friedel-Anderson virtual–bound-state model, has been applied to both dilute and concentrated Ce systems.[2-6] Central to most of these discussions were the ideas that the Ce $4f$ level (a) is within 0.1 eV of the Fermi energy (E_F), (b) has a hybridization width (Δ) of about 0.02 eV, and (c) moves to and through E_F with decreasing volume.[2-4] These treatments have been used in analyses of magnetic, volumetric, and transport properties.

Objections to these models and/or their choice of parameters, in the case of elemental Ce, have been made on such diverse grounds as photoemission,[7-9] positron annihilation,[10] and Compton-scattering experiments,[11] melting-point arguments,[12] and cohesive-energy arguments.[13] Of particular importance, then, is a direct measure of the $4f$ binding energy in α-like or γ-like Ce compounds and an identification of its volume dependence and degree of hybridization.

In this paper we report photoelectron-spectroscopy experiments on $CeAl_2$, $LaAl_2$, and "chemically compressed" alloys of $CeAl_2$ using synchrotron radiation. Our results address several problems in the previous Anderson-model treatments in a much more direct way than has been done previously.[7-13] Specifically, we find that our re-sults are incompatible with previous notions of the $4f$-level position and movement with volume [(a) and (c), above]. Moreover, combining our photoemission results with extensive transport data yields a drastically different Anderson-model estimate of the $4f$-level width than previously postulated [(b), above]. Finally, as we will show, if one wishes to retain Anderson-model ideas to explain the volume-dependent magnetic properties of $CeAl_2$, one must rely on $4f$-level broadening rather than on a shift in $4f$ binding energy with volume.

The cubic Laves-phase compound $CeAl_2$ is one of the most thoroughly studied Ce compounds.[14] For our purposes, its most important properties are (i) it has a well-established "γ-like" phase at ambient pressure,[14] (ii) it transforms to a volume-collapsed "α-like" phase above 7% volume compression,[15,16] and (iii) the role of the Kondo effect in its "γ-like" phase has been well characterized.[14,17,18]

In order to determine the position of the Ce-$4f$ level in this fascinating system, we have performed photoemission studies as a function of photon energy.[19] Studies of $CeAl_2$ and $LaAl_2$ under identical experimental conditions have made it possible to identify unambiguously the $4f$ contribution in $CeAl_2$. Furthermore, the $h\nu$ dependence of this $4f$ feature is dramatic and can be used to isolate the $4f$ contribution from the valence-band features.

In Fig. 1, we show photoelectron-energy distribution curves (EDC's) for $CeAl_2$ and $LaAl_2$ measured at several photon energies between 10 and 50 eV. As shown, at 10 eV, where the $4f$ cross section is small, the EDC's are effectively identical for the two compounds. By $h\nu = 30$ eV,
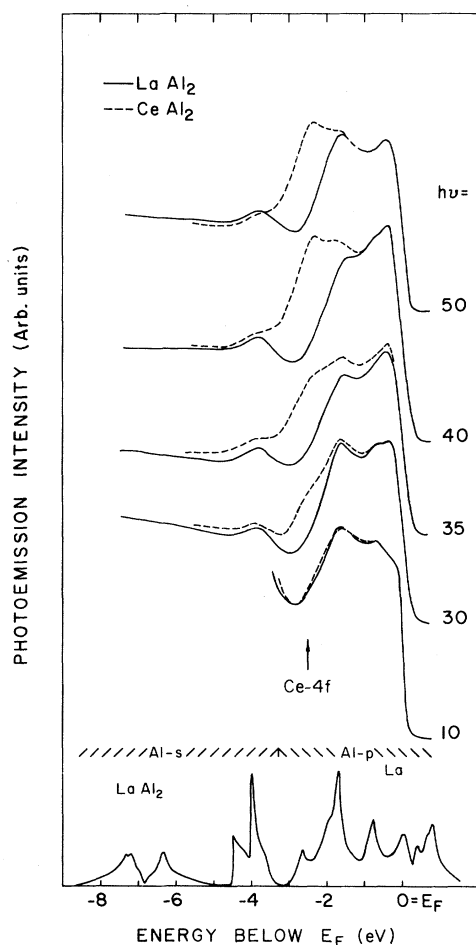
FIG. 1. Photoemission-energy distribution curves for $CeAl_2$ (dashed lines) and $LaAl_2$ (solid lines) at various photon energies. The identification of Al s, Al p, La d, and Ce d emission is on the basis of the band calculations of Ref. 20 and the density of states shown at the bottom. We ascribe the enhanced intensity of $CeAl_2$, relative to $LaAl_2$ (Ref. 20), centered at -2.55 eV to Ce $4f$ emission.

the EDC's clearly show a new structure in $CeAl_2$ at -2.55 eV relative to E_F. This structure becomes increasingly prominent at higher photon energies. *We identify this structure as the Ce $4f$ level by comparison to $LaAl_2$ and by the energy dependence of its cross section.* The other features in the emission spectra can be correlated to features in the density of states, e.g., that calculated by Hasegawa and Yanase[20] shown in Fig. 1. The overall agreement is excellent.

In γ-like Ce systems, including $CeAl_2$, a strong antiferromagnetic $4f$-electron–conduction-electron exchange (the Kondo effect) dominates the magnetic properties of the system.[2] This inter-

action can be related, through the Anderson model,[2,21] to the position of the $4f$ level in the conduction bands and $4f$–conduction-band coupling. Within this model, the Kondo temperature T_K (the characteristic energy of this exchange interaction) can be written as (see Ref. 21)

$$T_K = T_B \exp(-|E|\pi/2\Delta). \quad (1)$$

Here T_B is the conduction-electron bandwidth, E is the energy of the $4f$ level relative to E_F, and Δ is the hybridization width.[21,22] Applying these ideas to $CeAl_2$, where it is estimated that $T_K \simeq 5$ K (Ref. 14) and $T_B \simeq 5 \times 10^4$ K,[23] one finds that $E/\Delta \simeq -5.9$. In the past it was assumed that a typical value for Δ would be[2] $+0.02$ eV, thereby leading to the estimate[2] of $E \sim -0.1$ eV. *If, on the other hand, we use our spectroscopic value of $E = -2.55 \pm 0.1$ eV we must have $\Delta \sim 0.43$ eV to explain the observed magnetic properties in terms of the Anderson model.* While we do not claim that the photoemission width is this hybridization width we shall see below that they are numerically very close.

The change in the binding energy of the $4f$ level upon approaching an α-like state is as important as its absolute value. Motivated by the known transition of $CeAl_2$ to an α-like state for volume compressions in excess of 7% (reduced volumes below 0.93),[15,16,24] we have extended our measurements to include the "chemically compressed" compounds $Ce_{0.6}Y_{0.4}Al_2$ and $Ce_{0.6}Sc_{0.4}Al_2$. The effective unit-cell volumes (relative to $CeAl_2$) of these compounds are respectively 0.968 and 0.942. The more compressed compound ($Ce_{0.6}Sc_{0.4}Al_2$), it should be noted, is very close to the low-volume stability limit of the γ-like phase in this system.[15,16,24]

The $h\nu$ dependence in the experimental emission spectra of these compounds was similar to that of $CeAl_2$. Accordingly, we show in Fig. 2 only the spectra for $h\nu = 40$ eV for $CeAl_2$, $Ce_{0.6}Y_{0.4}Al_2$, and $Ce_{0.6}Sc_{0.4}Al_2$ superimposed in each case on the corresponding $LaAl_2$ curve. The Ce-$4f$ emission is still observed at -2.55 eV in both of these ternary compounds. In order to show it more clearly we have subtracted the normalized $LaAl_2$ EDC at 40 eV from that for $CeAl_2$, for $Ce_{0.6}Y_{0.4}Al_2$, and for $Ce_{0.6}Sc_{0.4}Al_2$. The difference curves, which reveal $4f$-derived emission, are shown in the inset of Fig. 2. In all three compounds the $4f$ level is centered at $E = -2.55$ eV with a full width at half maximum of about 1.10 eV. *Therefore, within our resolution, we find that the Ce $4f$ binding energy remains constant even up to*
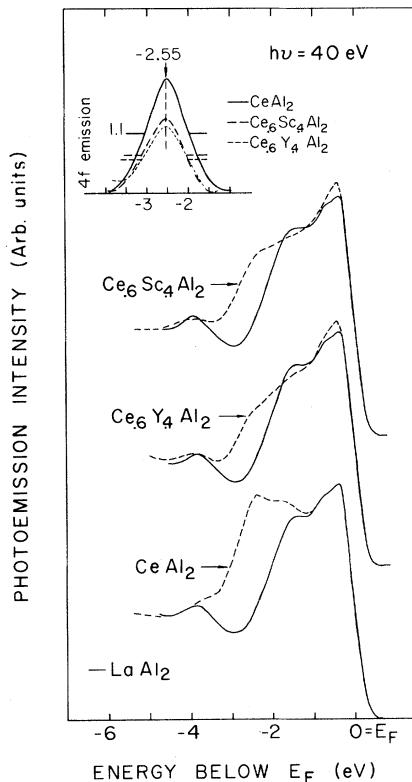
FIG. 2. The $h\nu = 40$ eV EDC for $CeAl_2$, $Ce_{0.6}Y_{0.4}Al_2$, $Ce_{0.6}Sc_{0.4}Al_2$, and $LaAl_2$ (dashed lines). Difference curves for EDC's of $CeAl_2$, $Ce_{0.6}Y_{0.4}Al_2$, and $Ce_{0.6}Sc_{0.4}Al_2$ with respect to $LaAl_2$ for $h\nu = 40$ eV are shown in the inset and reveal the $4f$ emission.

the low-volume stability limit of the γ-like phase in $CeAl_2$.

In the $Ce_{1-x}Sc_xAl_2$ system, a nonlinear but continuous volume collapse, with increasing x for $x > 0.5$, has been observed.[24] Since our measurements indicate that there is no $4f$ binding-energy shift precursive to this continuous volume collapse, the $4f$ binding energy should still be 2.55 eV when the collapse first starts. *Consequently our results strongly argue against a model in which the volume collapse in the Ce compound is explained by the 4f level simply moving to and through E_F.*

The volume dependence of the $4f$ binding energy (E) has been used previously, along with Eq. (1), to explain the volume dependence of T_K in a number of γ-like Ce systems.[2,3] With T_B held constant in Eq. (1), a change in volume leads to

$$\delta[\ln T_K] = (\tfrac{1}{2}\pi)\,\delta(E/\Delta). \tag{2}$$

For $CeAl_2$ the volume dependence of the Kondo

temperature has been extensively studied in "chemically compressed" alloys of the form $Ce_{1-x}R_xAl_2$, with $R = La$,[25] Y,[18,24] Sc,[24] and $La_{1-y}-Y_y$.[17,24] From these studies it is known that T_K increases by a factor of about 6 on going from $CeAl_2$ to $Ce_{0.6}Sc_{0.4}Al_2$ and hence, by Eq. (2), $\delta(E/\Delta) \simeq 1.1$. Assuming Δ remains constant with the value 0.5 eV (the value which we proposed earlier) implies $\delta E = 0.55$ eV upon 40% $ScAl_2$ substitution. Our photoemission results, on the other hand, show no measurable change in E. *Therefore the Kondo-temperature change cannot be explained by a change in 4f binding energy.*

Let us now inquire what change in the $4f$ hybridization width, Δ, would be required to explain the observed behavior of T_K. Holding E constant, in Eq. (2), as motivated by our photoemission results, yields

$$\delta\ln(T_K) = -\tfrac{1}{2}\pi(E/\Delta)\,\delta\Delta/\Delta. \tag{3}$$

For $Ce_{0.6}Sc_{0.4}Al_2$ and $Ce_{0.6}Y_{0.4}Al_2$, Eq. (3) requires that $\delta\Delta \simeq 0.08$ eV to explain the sixfold increase in T_K. A width increase of this magnitude is consistent with our photoemission results. *Therefore, if one wishes to retain Anderson-model ideas to explain the volume dependence of T_K, our results favor a mechanism where decreasing volume increases the 4f hybridization width or, in general, Δ increases as the α-like state is approached.*

Our study is, to the authors' knowledge, the first attempt to quantitatively correlate photoemission results with the bulk magnetic and transport properties of a Ce system.[26] In so doing we have been lead to critically reevaluate the key parameters in the Anderson model, as applied to $CeAl_2$. Our observation that the $4f$ binding energy is volume insensitive in "chemically compressed" alloys of $CeAl_2$ has forced us also to question the mechanisms traditionally used in Anderson model descriptions of the evolution from "γ-like" to "α-like" behavior in Ce systems. We are presently pursuing photoemission studies of other Ce systems to determine systematic variations in $4f$ binding energy, $4f$ binding width, and relaxation effects.

Note added.—Our results on $CeAl_2$ are in good agreement with those of Allen *et al.*,[27] despite their use of higher photon energies and of a dramatically different background-subtraction technique. Moreover, for a number of other Ce compounds, Allen *et al.* have independently reached general conclusions very similar to our own.

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