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Optical properties of CeAl₂ and LuAl₂

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Abstract. The optical properties of CeAl₂ and LuAl₂ were investigated in the 0.04–4.5 eV region using ellipsometry and reflectivity measurements. At low energies, the optical conductivity for CeAl₂ showed two structures at about 0.1 and 1 eV, which were not found for LuAl₂. These structures can be understood as due to interband transitions, $d \rightarrow f$ and $f \rightarrow d$, between band-like 4f and 5d character near the Fermi level. At higher energies above 1 eV, the optical conductivity spectra for both compounds show similar behaviours with structures at about 2 eV for both compounds and a structure at about 3 eV for CeAl₂ and at about 4 eV for LuAl₂. The 2 eV structures for both compounds can be assigned as $d \rightarrow p$ transitions with the p character existing just above the f bands and the 3 and 4 eV structures may contain $s \rightarrow p$ transitions in addition to $d \rightarrow p$ transitions, with the s character existing near the Fermi level through hybridization with the d bands.

The electronic structures of Ce and its compounds have been under a great deal of theoretical and experimental investigation because of their various electric, magnetic and optical properties caused by the interaction of the 4f electrons with their environments. For example, valence band spectra of Ce [1] and some of its compounds [2] obtained from ultraviolet photoemission spectroscopy measurements show two peak structures associated with the 4f electrons, one near the Fermi level E_F and another about 2 eV below E_F , which gives crucial evidence for the coexistence of the two configurations (a core-like state and a band-like state) that the 4f electrons can occupy. Here, the most important physical quantity in describing the solid Ce system by the above concept of intermediate valency is the wavefunctions of the 4f states. The 4f wavefunctions in the solid state Ce are radially more extended than in atomic Ce, having some degree of itineracy because of the overlap between neighbouring Ce sites, producing narrow 4f bands near E_F . Also, owing to near degeneracy in the energy of the 4f bands with other valence bands (e.g. 5d and 6s), hybridization is effective to give a more 4f-type bandwidth.

The itineracy of the 4f electrons in elemental Ce is known to be the most important factor in explaining the physical difference between the two phases in Ce, the γ -phase with higher volume and local magnetic moment with the susceptibility following a Curie–Weiss law and the α -phase with a lower volume (volume collapse by 17%), loss of local magnetic moment, and superconductivity [3]. As in elemental Ce, competition between core-like and band-like behaviour of 4f electrons is an important factor in determining the physical properties of various Ce compounds.

CeAl₂ is one of the well studied Ce compounds crystallizing in the cubic Laves (MgCu₂) structure in which Ce atoms form a diamond sublattice [4]. The nearest-neighbour distance between Ce atoms is smallest in the MgCu₂ structure compared with other types

of compound [5] so that in CeAl_2 , which has a Ce–Ce nearest-neighbour distance closer to that of $\alpha\text{-Ce}$, 4f–4f overlap becomes significant to give a finite 4f bandwidth as in $\alpha\text{-Ce}$. CeAl_2 has been paid particular attention because of its heavy-electron behaviour near the Fermi surface, e.g. large electronic specific-heat coefficient [6] and resistance anomalies [7], which indicate the existence of significant 4f character near E_F .

In the following, we report the optical properties of CeAl_2 and LuAl_2 studied by ellipsometry and reflectivity measurements. LuAl_2 was used as a reference material for resolving optical transitions involving the 4f states in CeAl_2 located near E_F because the 4f states in LuAl_2 are completely filled and located well below E_F [8] so that low-energy (less than 5 eV) optical spectra could not contain excitations involving them. Both samples were polycrystals and were mechanically polished with abrasives, the final grade being a paste of alumina of 0.05 μm diameter. Unlike CeSn_3 , CeAl_2 and LuAl_2 are not very reactive; therefore all the optical measurements were performed in the air. Ellipsometry measurements were done with a rotating-polarizer–analyser ellipsometer to determine the dielectric functions ($\epsilon = \epsilon_1 + i\epsilon_2$) of the samples at room temperature in the 1.5–4.5 eV region. Near-normal-incidence reflectivity measurements were carried out at 0.04–4.1 eV using two spectrometers (0.04–0.5 eV and 0.5–4.1 eV). We obtained the dielectric functions of the two compounds in the low-energy region (0.04–1.5 eV) by Kramers–Kronig analyses of the reflectivity data. For energies larger than 4.5 eV up to 20 eV, reflectivities were assumed to decrease as ω^{-p} ($p \leq 2$) and for still higher energies as ω^{-4} , where p is an adjustable parameter to produce the resultant dielectric functions, which differ by less than $\pm 5\%$ in magnitude from the ellipsometry data in the 1.5–4.5 eV region. For energies below 0.04 eV, reflectivities were assumed to increase by $1 - A\omega^{1/2}$. The peak positions of the structures for both compounds were not sensitive to values of p .

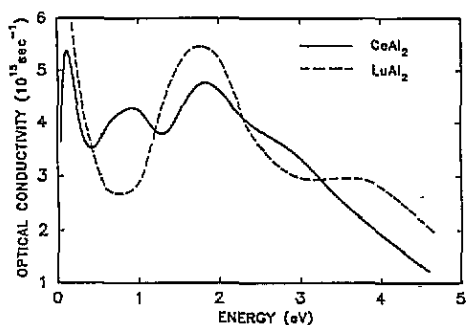


Figure 1. Real part of the optical conductivities of CeAl_2 and LuAl_2 . Note that the zero of the optical conductivity is suppressed.

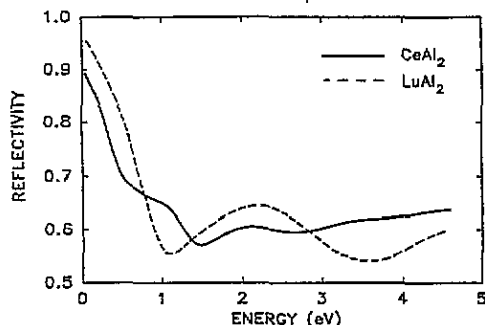


Figure 2. Normal-incidence reflectivity spectra of CeAl_2 and LuAl_2 . Note that the zero of the reflectivity is suppressed.

Figure 1 exhibits the real part of the optical conductivities ($\sigma_1 = \omega\epsilon_2/4\pi$) of CeAl_2 and LuAl_2 , in which low-energy structures can be resolved better than in the imaginary part of the dielectric function because of its slower ω^{-1} divergence at low energies compared with ω^{-2} divergence for the dielectric function. The reflectivity spectra for both compounds used to construct σ_1 are shown in figure 2. It is seen that the optical conductivity spectra for both compounds have similar interband structures at about 2 eV and at higher energies (3 eV for CeAl_2 and 4 eV for LuAl_2). At lower energies, CeAl_2 shows two interband peaks at about 0.1 and 1 eV, while LuAl_2 shows no such structures in the same energy region.

The valence band electronic structure of $CeAl_2$ was theoretically investigated from band-structure calculations [5, 9, 10]. In [10], the band structure of $CeAl_2$ was calculated, treating the 4f electrons as in core states. However, the density of states at E_F calculated from the band structure was too small (only about 5%) compared with the experimental value [6]. When the 4f electrons were treated as in band states, the density of the 4f character is peaked just above E_F [5] so that the density of states at E_F becomes larger by a factor of three than when treating the 4f electrons as in core-like 4f states.

The difference between the electronic structures of $CeAl_2$ and $LuAl_2$ is the existence of band-like occupied and unoccupied 4f character near E_F in $CeAl_2$, which can contribute to interband transitions as initial or final states of the transitions, while no band-like 4f character exists in $LuAl_2$ owing to the strongly localized nature of completely filled Lu 4f states [8] in $LuAl_2$. Therefore, the existence of the 0.1 and 1 eV structures in $CeAl_2$ can be understood as due to interband transitions involving band-like 4f character as initial or final states of the transitions, the possible electric dipole transitions being $d \rightarrow f$ and $f \rightarrow d$ transitions.

Because of the flat nature (weak dispersion) of the 4f bands in $CeAl_2$ obtained from a band-structure calculation [5] it is possible to assign the main contributions to the 0.1 and 1 eV structures. The 4f character in $CeAl_2$ is peaked just above E_F so that the density of 5d character is expected to be small near E_F . Hence, the 0.1 eV structure is temporarily assigned as mainly due to the interband transitions between occupied 5d character just below E_F and unoccupied 4f character just above E_F ($d \rightarrow f$ transitions). On the other hand, the 1 eV structure can be contributed by both $d \rightarrow f$ and $f \rightarrow d$ transitions owing to the well dispersed nature of the 5d bands across E_F . The interband structures located at higher energies for both compounds (2 and 3 eV for $CeAl_2$ and 2 and 4 eV for $LuAl_2$) are expected to have similar origins because the band structures of the two compounds are similar except for the existence of the 4f bands near E_F in $CeAl_2$. For the 2 eV structures for both compounds the p character hybridized with and located above f bands is expected to be involved as final states of the interband transitions, i.e. $d \rightarrow p$ transitions. The 3 eV structure for $CeAl_2$ and 4 eV structure for $LuAl_2$ may involve contributions from the s character hybridized with d bands and located closer to E_F as initial states, i.e. $s \rightarrow p$ transitions in addition to $d \rightarrow p$ transitions.

Low-energy interband structures below 1 eV were also found in the optical spectra of $CeCu_6$ [11] and $CePd_3$ [12, 13]. In [11], the optical conductivity for $CeCu_6$ showed interband structures at about 0.1 and 0.3 eV at 6 K while, for $LaCu_6$, only a structure at about 0.1 eV was resolved. At higher energies above 2 eV, both $CeCu_6$ and $LaCu_6$ showed similar behaviours with structures at about 3 and 5 eV for both compounds. In [12, 13], two low-energy peaks were found for $CePd_3$ at 0.25 eV and 0.8 eV, which are close in energy to the two low-energy peaks in $CeAl_2$ (0.1 eV and 1 eV) and were assigned as $d \rightarrow f$ and $f \rightarrow d$ transitions, respectively, in [13]. The existence of the band-like 4f states near E_F for the above Ce intermetallic compounds can cause interband transitions involving these states, which can be identified by comparing the optical dielectric functions of the Ce compounds with those of other rare-earth compounds having different 4f-state properties.

In summary, the optical conductivity of $CeAl_2$ has two additional structures at about 0.1 and 1 eV, while that of $LuAl_2$ has only two structures at about 2 and 4 eV, for which $CeAl_2$ also has corresponding structures at about 2 and 3 eV. The difference between the electronic structures of $CeAl_2$ and $LuAl_2$ is that $CeAl_2$ has band-like 4f states near E_F owing to a relatively better extended nature of its 4f wavefunctions than $LuAl_2$ which has completely filled and well localized 4f states located well below E_F . Other parts of the valence bands of the two compounds are expected to be similar owing to the flat nature

and weak hybridization with s-p-d bands of the f bands of CeAl₂. From a comparison of the electronic structures of the two compounds the 0.1 and 1 eV structures of CeAl₂ can be assigned as the interband transitions involving the Ce f character existing near E_F , d → f and f → d transitions. The structures at about 2 eV found for both compounds are expected to be due to d → p transitions with the p character appearing just above the f bands and the structures in the 3–4 eV range for both compounds may involve the s character located close to E_F owing to s-d hybridization, causing s → p transitions.

Acknowledgments

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