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HAL Id: jpa-00222354
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Submitted on 1 Jan 1982

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MAGNETIC ORDERING AND ELECTRONIC STRUCTURE OF CeAl$_2$

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Résumé. CeAl$_2$ a suscité un intérêt considérable en raison de ses propriétés inhabituelles, en particulier la structure antiferromagnétique modulée dont il a été proposé qu'elle résulte d'une compétition mettant en jeu le phénomène de compensation de Kondo. Dans cet article nous présentons pour CeAl$_2$ les résultats d'un calcul de bande self consistant, tenant compte de la polarisation de spin et utilisant la méthode des orbitales de type muffin tin (LMTO). Dans l'état paramagnétique la bande f du cérium a une largeur d'environ 1 eV. Bien que située essentiellement au-dessus de $E_F$, cette bande est occupée par l'électron 4f et la densité d'état au niveau de Fermi est très forte. D'après le calcul, l'état ferromagnétique n'est pas stable. Par contre, l'état antiferromagnétique est stable avec un moment magnétique de 0.88μ$_B$ par atome de cérium, en très bon accord avec les mesures de neutrons de Barbara et al. Etonnamment, la structure antiferromagnétique modulée semble reliée à l'existence de zones parallèles importantes dans la surface de Fermi de LaAl$_2$ (c'est à dire lorsqu'il n'y a pas d'électron 4f) plutôt que dans celle de CeAl$_2$.

Abstract. CeAl$_2$ has attracted considerable attention because of its unusual properties including a proposed competition between Kondo compensation and anti-ferromagnetic spin-density wave ordering observed at low temperatures. Here we present results of a self-consistent spin-polarized LMTO band study of CeAl$_2$. In its paramagnetic state the Ce-f band is about 1 eV wide and, although principally above $E_F$, it accommodates the additional 4f electron when compared to LaAl$_2$ and gives rise to a very high DOS at $E_F$. The ferromagnetic state is found not to be stable. By contrast, the anti-ferromagnetic state is found to be stable with a magnetic moment of 0.88μ$_B$ per Ce atom in very good agreement with neutron measurements by Barbara et al. Surprisingly, the anti-ferromagnetic spin-density ordering appears to be related to nesting features in the underlying Fermi surface in LaAl$_2$ (i.e. no 4f electron) rather than that of CeAl$_2$.

Cerium and its compounds display various interesting properties ascribed to the behavior of its f-electron. One can mention Kondo-like Ce systems, compounds with developed spin-density waves, heavy fermion systems, ordinary ferromagnetism, and superconductivity. The cubic laves, or C15, phase of CeAl$_2$ which exhibits anti-ferromagnetic spin-density wave ordering has been extensively studied. This magnetization structure determined by means of neutron scattering [1] provides useful guidance and information for direct comparison with predictions of energy band theory. The cubic laves, or C15, phase of CeAl$_2$ which exhibits anti-ferromagnetic spin-density wave ordering has been extensively studied. This magnetization structure determined by means of neutron scattering [1] provides useful guidance and information for direct comparison with predictions of energy band theory. Other C15 compounds with Ce exhibit ferromagnetism or superconductivity, and hence theoretical studies of Ce C15 compounds may give important insights into the behavior of the f-electrons. In addition, the C15 structure with 6 atoms per unit cell is a close-packed structure which permits the use of simpler computational techniques. The localized nature of most rare-earth f-electron systems make a local loosely coupled atomic multiplet structure the most useful way of describing them. But Ce with only one occupied f-electron of greater radial extent is on the limit of itinerant behavior and has been studied successfully by band structure calculations [2]. And, as we will see, our band results for CeAl$_2$ are realistic and provide useful insights into the nature of f-electron bonding in this material.
The energy band structures were determined self-consistently using the linear muffin tin orbital (LMTO) method [3, 4] with fully relativistic core functions re-calculated in each iteration and a semi-relativistic approach (i.e. neglecting the spin-orbit coupling [5]) for the valence states. The basis-set included s-, p-, d- and f- orbitals ($l_{\text{max}} = 3$) for the Ce sites, s-, p- and d- orbitals ($l_{\text{max}} = 2$) for the Al sites and with one $l$-number higher in the three centre terms to improve convergence. The method utilizes spherically symmetric potentials within overlapping Wigner-Seitz (WS) spheres. The eigenvalue problem is corrected for the overlapping geometry which further improves the $\lambda$-convergence. The band structures were determined in 85 independent k-points in the irreducible Brillouin Zone (IBZ) - a $\pi/4a$ cubic mesh. The local density formalism of Hedin, et al. [6] was used to incorporate the exchange and correlation contribution to the potential. In the spin-polarized calculations, the local spin density formalism of Gunnarsson and Lundqvist [7] has been added to give two potentials, one for each spin. In the ferromagnetic configuration, the calculation included an applied magnetic field in order to determine the magnetic response and susceptibility [8]. The self-consistent calculations for CeAl$_2$ were more complex than other compounds due to the extreme sensitivity of the f-band at the Fermi energy.

The results obtained were compared to those obtained in separate calculations for YAl$_2$ and LaAl$_2$ in order to understand the effects of additional f-electrons. A more extensive report of these results will be given elsewhere. Paramagnetic results show that about 1.1 Ce f-electron is occupied, which is almost one more electron than found in LaAl$_2$. All other partial occupation numbers are very similar in the two materials. Their bandstructures are very similar, except for the f-band region, which in CeAl$_2$ starts just below $E_F$ (~0.15 eV) and is about 1 eV wide (cf. Fig. 1). This leads to a very high density-of-states (DOS) at $E_F$ of 12.5 states per eV and unit cell, dominated by Ce-f (~60%). (Still the extremely high electronic specific heat coefficient correspond to an electron-phonon coupling of 7-8

![Figure 1. The CeAl$_2$ ferro-magnetic density-of-states. The insert shows the behavior near $E_F$.](image)
if one uses the calculated DOS.) The DOS at $E_F$ in LaAl$_2$ shown in Fig. 2 is much lower, 4.4 (eV-cell)$^{-1}$ and has very little La-f character. The other partial DOS values show only a few similarities with those in CeAl$_2$ near $E_F$. The fermi surface (FS) structures in the two compounds are completely different and the FS in CeAl$_2$ is extremely sensitive to small shifts of $E_F$, as would be expected for such flat bands.

In the ferromagnetic calculations an applied magnetic field of 2mRy (which on an experimental scale is an enormous field of 4.5 MG) is included. For CeAl$_2$, the exchange splitting near $E_F$ amounts to 5 mRy, corresponding to an exchange enhancement of 2.5. The magnetic moment is 0.44$\mu_B$ per unit cell, of which about 80 percent is on the two Ce atoms. The values for LaAl$_2$ are smaller: 1.4 for the exchange enhancement and a total moment of 0.05$\mu_B$. Still, the values for CeAl$_2$ are not large and an intrinsic stable ferro-magnetic configuration seems unlikely. In fact, further iteration with the field removed leads to an immediate reduction of the moment suggesting that it will vanish.

The neutron scattering experiments by Barbara, et al., [1] showed a complex anti-ferromagnetic (AF) structure in CeAl$_2$ below the Néel temperature at 3.8 K. The two Ce atoms at $(0,0,0)$ and $(\%\%,\%\%)$ have opposite spin alignment with a modulation in the [110] direction. The maximum moment within a [110]-plane is 0.89$\mu_B$ per Ce atom. Whereas the modulation structure is too complicated to include in a theoretical study, it is a manageable calculation to include the anti-ferromagnetic configuration i.e. to assign opposite spin for the two Ce atoms in the ordinary unit cell. One then has three inequivalent potentials per unit cell: the two Ce plus Al (which cannot polarize due to symmetry). The initial configuration assumed 0.25$\mu_B$ per Ce (anti-ferromagnetic) and the self-consistent calculation proceeded in the same manner as the ferromagnetic calculation but with no external fields applied.

The final magnetic moment is found to be 0.88$\mu_B$ per Ce in excellent agreement with experiment. The f-band is now split by about 1 eV between the majority and

![Figure 2. The LaAl$_2$ ferro-magnetic density-of-states. The insert shows the behavior near $E_F$.](image-url)
minority bands (referring to one Ce atom), both being $\frac{1}{2}$ eV wide. Clearly the f-levels interact very differently with the remaining band-like levels according to whether they are in an anti-ferromagnetic or paramagnetic (forced ferromagnetic) configuration. As indication that this is so, we note that in the forced ferromagnetic case the Ce and Al moments are proportional to the local DOS values. This indicates that there is large hybridization between Ce and Al states. From a Stoner model for compounds one knows that low local DOS, such as that for Al, strongly reduces the exchange enhancement or excludes magnetism [9]. On the other hand, it is advantageous for magnetism if a spin splitting can occur only for the f-levels which have a large local DOS, such as for the Ce bands. This cannot happen in the ferromagnetic configuration where the Ce and Al bands were found to be coupled and hybridized to split almost equally in an applied field. However, the AF structure considered here has by symmetry zero moment and (zero spin splitting) on Al, whereas the two Ce atoms can have large (opposite) spin splittings. Thus decoupled Ce and Al bands, such as in the AF case, are favorable for a magnetic transition and one can understand why the AF configuration is more likely than the ferromagnetic configuration in this CeAl$_2$ structure. On the other hand, the Ce-f electron and its localization is certainly also of importance, since the above-mentioned arguments apply also for the nearly ferromagnetic C15 compounds TiBe$_2$ and ZrZn$_2$ with high/low local DOS on the Ce/Al sites [9,10]. However, the difference is that these compounds have itinerant d-states whereas in CeAl$_2$, the localized Ce-f states have limited interaction between different Ce sites and their spins can align rather independently of each other.

In order to understand the complex modulation of the magnetization structure in CeAl$_2$ one might look for nesting features in the FS. However, the complex paramagnetic FS for CeAl$_2$ shows no interesting features and is very sensitive to uncertainties in $E_F$ due to the very flat f-bands. Instead it is interest-

![Figure 3](image_url)

Figure 3. The anti-ferromagnetic density-of-states for CeAl$_2$. The insert shows the behavior near $E_F$. The two spin DOS functions are identical but the two f-peaks correspond to opposite spin orientation on the two Ce sites.
ing to note that the FS of LaAl\(_2\) (which has a bandstructure similar to that of CeAl\(_2\), just below \(E_F\)) shows evident strong nesting structures, both in the [110] and [111] directions, which seem relevant for the CeAl\(_2\) magnetization structure. The flat FS piece half-way between \(\Gamma\) and \(L\) fits well to the Ce-Ce separation along [111]. A slight displacement of the nesting piece on the \(\Gamma\) to \(K\) line to be not quite half-way, could be associated with the modulation along [110] in CeAl\(_2\). Thus it is tempting to regard the f-electron in CeAl\(_2\) as sufficiently localized so it does not participate in the formation of the FS. Instead it appears to be the itinerant conduction electrons, like those for LaAl\(_2\), which sets up the FS and its nesting properties. This in turn, leads to peaks in the generalized susceptibility, \(\chi(q)\), and to the observed spin density wave ordering at the \(q\) value at which \(\chi(q)\) has its maximum. Thus different Ce compounds with different structure and FS, may well have different magnetization structure.

There are a number of features which need be considered when interpreting these results: 1) The AF moment is reasonably correctly given; 2) The total f-orbital DOS width (neglecting gaps) in the paramagnetic, ferromagnetic, and AF configuration does not change dramatically; 3) The Fermi surface of LaAl\(_2\) exhibits nesting features appropriate to magnetic ordering in CeAl\(_2\); and 4) In the ideal AF configuration, symmetry does not permit a net moment on the Al site. If one uses the traditional logic applied to rare-earth systems and considers Ce to be trivalent and LaAl\(_2\) to have all the itinerant electron properties, then the f-electron in CeAl\(_2\) would occupy an otherwise unfilled core-like atomic shell state. The nesting feature of LaAl\(_2\) produces a peak in the generalized response function \(\chi(q)\) of the itinerant states which couples the moment of the f-orbitals. From such a model, one would expect the band calculation to do quite well for the resulting moment provided one can ignore spin-orbit coupling and orbital effects. Further, the energy of the system would be lowered because, in relieving the instability caused by the nesting features, the occupied states would be lowered in energy; the simultaneous raising of the unoccupied states would not affect the energy of the system. Energy is also gained, of course, from the exchange-correlation functional by polarizing the system. The mechanism of polarization induced localization [11] applied to the volume collapse under pressure of Am [12] is not applicable here as can be seen from the "constant bandwidth" in all three system configurations. Besides the Ce separation is too large to ever permit a direct f interaction [13]. The f-orbital system, although no doubt slightly contracted and thereby somewhat more weakly coupled in the polarized states, remains coupled into the conduction electron system. There is no net moment coupling through the aluminums because symmetry does not permit a net Al moment in the idealized commensurate configuration.

In summary, we have shown that an anti-ferromagnetic state is stable in CeAl\(_2\) and is favored over the ferromagnetic state. The calculated Fermi surfaces in LaAl\(_2\) and CeAl\(_2\) suggest that the f-electron in Ce is localized and does not participate in the transport properties of \(\chi(q)\) associated with Fermi surface. The Fermi surface of LaAl\(_2\) has nesting properties which correspond reasonably well to the spin density wave ordering seen in CeAl\(_2\). A determination of the Fermi surface in CeAl\(_2\) by deHaas-van Alphen appears necessary in order to clarify the behavior of the f-electrons.


References.