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By

T. Jarlborg
DPMC Universite de Geneve, CH-1211, Geneve, Switzerland

A. J. Freeman
Dept. of Physics, Northwestern University, Evanston, IL 60301

and

D. D. Koelling
Argonne National Laboratory, Argonne, Illinois 60439

Materials Science and Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

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MAGNETIC ORDERING AND ELECTRONIC STRUCTURE OF CeAl_2 *

T. Jarlborg, DPMC Université de Genève, CH-1211, Genève, Switzerland
A.J. Freeman, Dept. of Phys., Northwestern University, Evanston, IL 60201 USA
D.D. Koelling, Argonne National Laboratory, Argonne, Illinois 60439 USA

Abstract. CeAl_2 has attracted considerable attention because of its unusual properties including a proposed competition between Kondo and anti-ferromagnetic spin-density wave ordering observed at low temperatures. Here we present results of a self-consistent spin-polarized LMT0 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 $0.88\mu_B$ 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 .

density of states

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. 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 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 (LMT0) method [3, 4] with fully relativistic core functions recalculated 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 ($l_{\max} = 3$) for the Ce sites, s-, p-, and d- orbitals ($l_{\max} = 2$) 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 l-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

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 ($\sim 60\%$). (Still the extremely high electronic specific heat coefficient correspond to an electron-phonon coupling of 7-8 if one uses the calculated DOS.) The DOS at E_F in LaAl_2 shown in Fig. 2 is much lower, $4.4 (\text{eV-cell})^{-1}$ 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.

Figure 1. The CeAl_2 ferro-magnetic density-of-states. The insert shows the behavior near E_F .

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 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ have opposite spin alignment with a modulation in the $[1\bar{1}0]$ direction. The maximum moment within a $[1\bar{1}0]$ -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 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

Figure 2. The LaAl_2 ferro-magnetic density-of-states. The insert shows the behavior near E_F .

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 $\chi(\mathbf{q})$ 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 $\chi(\mathbf{q})$ 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.

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