4*f*-Band Magnetism in CeFe₂

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We explain the anomaly in the lattice constants of the series CeFe₂-CeNi₂ *quantitatively* in terms of 3*d*-4*f* hybridization rather than a valence change. CeFe₂ is calculated to be magnetic and is the first Ce compound for which self-consistent energy-band calculations yield the correct total moment (2.4μ_B/formula unit) including a contribution of $-0.4\mu_B$ from the 4*f* electrons. The calculated magnetization density and spin-resolved density of states, which are unique to itinerant-electron theory, may be verified in detail by magnetic form-factor and spin-polarized photoemission measurements.

The electronic structure of Ce and its compounds is a controversial subject. The standard model for 4*f* electrons in the rare-earth metals and their compounds is that an integral number of 4*f* electrons are localized on each rare-earth ion. This applies to both normal rare earths, where one 4*f* configuration of given occupation is stable, and to mixed-valent cases, where fluctuations between two 4*f* configurations with different integral 4*f* occupations take place. Thus electronic phase transitions in Ce and some of its compounds are often described in terms of either the Pauling-Zachariasen promotional model[1] or the Kondo lattice model,[2] both of which are consistent with the standard model of the rare-earth ion in solids. This is in sharp contrast to the way itinerant-electron theory, based upon local approximations to density-functional theory, has been successfully used to calculate the cohesive and magnetic properties of *d*-electron transition metals.[3]

However, the application of the standard model to some Ce systems has been questioned on thermodynamic[4] and structural[4,5] grounds, the best known example being the α-γ transition in Ce metal. *Ab initio* energy-band calculations yield approximately the correct lattice constant and paramagnetic ground state for α-Ce[5-7] and CeN,[8] but it is not generally accepted that this constitutes enough evidence for the itinerancy of the 4*f* electrons in these systems.

A convincing demonstration, at both bulk and microscopic levels, that the 4*f* states in Ce can form energy bands in some circumstances requires an *ab initio* calculation which not only yields known bulk ground-state properties correctly but also predicts microscopic quantities, preferably densities, that unambiguously arise from 4*f* itinerancy and can be measured. Since the charge density is not easily measured, we need a Ce compound with magnetic 4*f* electrons as the spin density is more accessible to experiment. CeFe₂ is such a compound and, as we shall show, neutron diffraction and spin-polarized photoemission are the experiments.

The cubic Ce*M*₂ Laves-phase intermetallic compounds (*M* = Fe, Co, Ni) have anomalously small lattice constants compared with those of the corresponding compounds of all other rare earths. This is illustrated in Fig. 1 where we have plotted the lattice constants of the trivalent rare-earth *R M*₂ compounds by giving Gd and Pr as examples, and including "trivalent cerium" which was extrapolated from data for the trivalent rare earths. The lattice constants decrease monotonically from *R*Fe₂ to *R*Ni₂, as they do for the Y*M*₂ compounds. Also plotted are the lattice constants of the Ce*M*₂ and U*M*₂ series both of which are anomalous with a minimum at *A*Co₂.
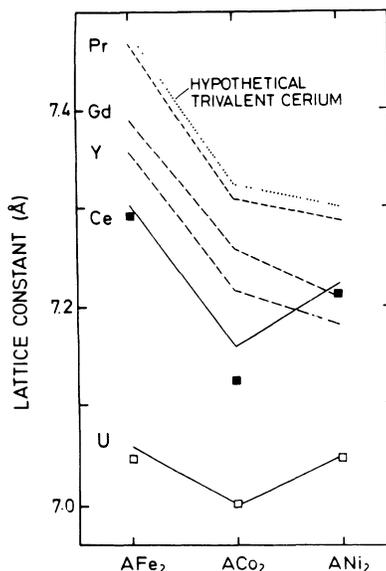
FIG. 1. The full and dashed lines connect experimental lattice constant data for the *A M*₂ systems (*A* = U, Ce, Y, and Gd; and *M* = Fe, Co, and Ni). The filled squares are the calculated lattice constants for Ce*M*₂ systems (present work) and we have included the results of earlier calculations (Ref. 9) for U*M*₂ systems for completeness.

We have made self-consistent linear muffin-tin orbit-al[10] calculations for the CeM_2 compounds in the same manner as described elsewhere.[9] The zero-temperature equation of state emerges quite naturally from such calculations in the atomic-sphere approximation,[11] and from it the calculated lattice constants which are also shown in Fig. 1. They agree with the measurements to within 0.5% and reproduce the anomalous minimum for $CeCo_2$. The minimum originates from $3d$-$4f$ hybridization, which gives rise to an earlier filling of the bonding bands than for a localized $4f$ rare-earth compound. If the $4f$ electrons were localized there would be no $4f$ contribution to the calculated equation of state; when we remove this contribution from our results the calculated lattice constants are close to the curve labeled "trivalent cerium." Thus itinerant-electron theory yields the correct lattice constants for the CeM_2 series.[12]

It has until now been necessary to explain the volume anomaly between $CeCo_2$ and $CeNi_2$ in terms of a valence change from 4 to 3.4.[13,14] However, L_{III}-edge measurements[15] indicate a constant valence of about 3.3 across the $CeFe_2$-$CeNi_2$ series. We find a $4f$ occupation number of about 1.15 for the three compounds, in agreement with the latter observations, and explain the volume anomaly quantitatively in terms of $3d$-$4f$ hybridization—thus resolving the problem.

The magnetic properties of the CeM_2 systems are similar to the corresponding YM_2 systems—$CeCo_2$ and $CeNi_2$ being paramagnets and $CeFe_2$ having an ordered moment—except that YFe_2 has a larger total moment[16] [$2.9\mu_B$/formula unit (f.u.)] than $CeFe_2$ ($2.3\mu_B$/f.u.) and a much higher Curie temperature (545 K compared to 235 K). The calculated densities of states (DOS), $N(E)$, and inverse of the Stoner parameter, I, for the three CeM_2 compounds are shown in Fig. 2. Only for $CeFe_2$ is the Stoner product[17] $IN(E_F)$ greater than 1, yielding itinerant-electron magnetism, and we obtain the magnetic instability in agreement with experiment. $CeCo_2$ is an enhanced paramagnet since the Stoner product is 0.95. Our calculated linear specific-heat coefficients, γ, are 14.7 and 10.5 mJ/mol K^2 for $CeCo_2$ and $CeNi_2$, respectively, compared with the measured values[18] of 21 and 11 mJ/mol K^2.

The spin-projected state densities, spin densities, and spin moments of $CeFe_2$ were then obtained from self-consistent spin-polarized calculations. Neither the partial Ce-$4f$ nor partial Fe-$3d$ state densities are displaced rigidly by polarization—a consequence of the changes in hybridization discussed below. We could not, therefore, have obtained the present results without a complete energy-band calculation. The calculated total spin moment of $\mu_s = 2.16\mu_B$/f.u. is composed of antiferromagnetically coupled moments of $1.43\mu_B$ per Fe atom and $-0.70\mu_B$ per Ce atom. The measured[19] total moment is $2.3\mu_B$/f.u. but in the absence of neutron-diffraction experiments there is no measured decomposition. The calculated Fe moment is almost entirely of $3d$ character,
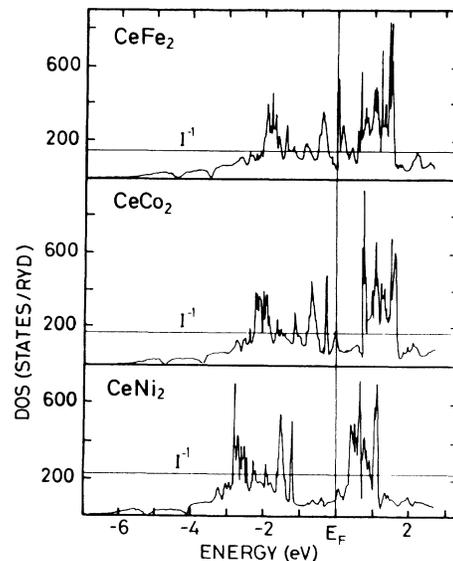
FIG. 2. Calculated state densities from self-consistent linear muffin-tin orbital calculations for CeM_2 systems. The horizontal lines are the inverse Stoner parameters. The Fermi energy is at zero.

whereas for Ce it is an almost equal mixture of $4f$ ($-0.4\mu_B$) and $5d$ ($-0.3\mu_B$) contributions. Although it is not central to our argument we have checked the importance of relativistic effects upon the moment by adding spin-orbit coupling to the linear muffin-tin orbital Hamiltonian and iterating to self-consistency as we have previously done for U compounds.[20] The result was that we obtained small but not negligible orbital contributions of $\mu_l = 0.08\mu_B$ to the Fe-$3d$ moment[21] and $\mu_l = 0.15\mu_B$ to the Ce-$4f$ moment. The spin contributions were changed slightly to $\mu_s = 1.41\mu_B$ for Fe and $\mu_s = -0.72\mu_B$ for Ce. The calculated total moment became $2.41\mu_B$, in agreement with experiment.

To the excellent agreement between itinerant-electron theory and experiment for the lattice constants of the $CeFe_2$-$CeCo_2$ systems, not least the minimum at $CeCo_2$, we have added a new feature for a Ce compound —agreement on the value of the total moment of $CeFe_2$. Further, the nature of the magnetism at the Ce site is uniquely associated with $4f$-band magnetism.

In RM_2 systems in general, the M-$3d$ states and R-$5d$ states hybridize strongly to form bonding and antibonding bands. When a moment develops at the M sites the energy of spin-up $3d$ states is lowered, reducing the $3d$-$5d$ hybridization for the spin-up states. The opposite effect occurs for the spin-down states and the induced $5d$ spin density is therefore antiparallel to the $3d$ spin density.[22] Thus, if we take $TbFe_2$ as the best known example, the $5d$ electrons polarize antiparallel to the $3d$ electrons, and, through a local ferromagnetic interaction, the spin of the $4f$ electrons aligns with that of the $5d$ electrons. In Tb this effect is reinforced by an orbital $4f$ contribu-

(a)

(b)
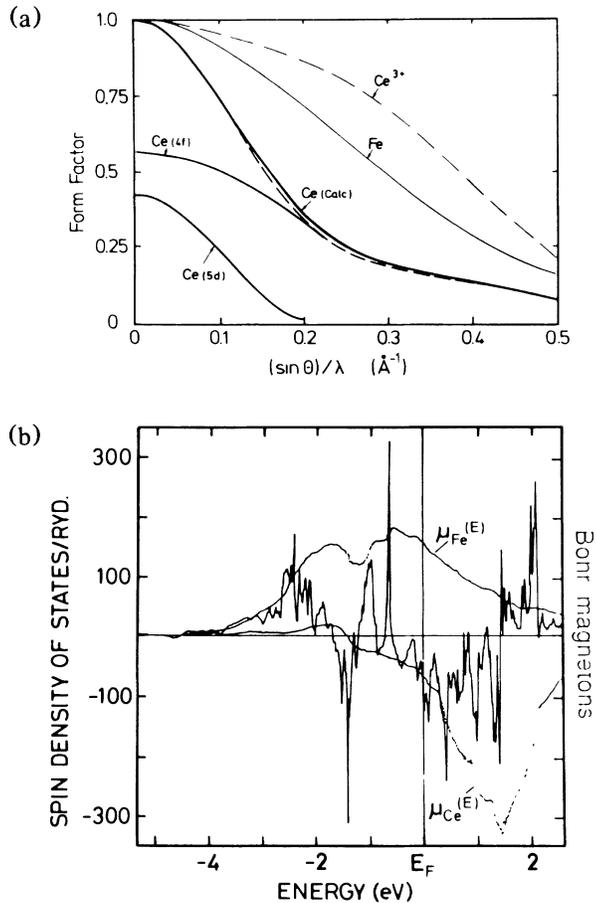
FIG. 3. (a) Magnetic form-factor analysis. The calculated form factor of Fe is normal. The normal ($4f$) form factor of Ce is marked Ce^{3+} (Ref. 23) and contains a large orbital contribution. The calculated Ce form factor of Ce in $CeFe_2$ is marked Ce(Calc) and is composed of $4f$ and $5d$ contributions which add to give Ce(Calc). All form factors, except the latter two contributions, are normalized to ease comparison. The dashed curve close to Ce(Calc) is the calculated spin-only Ce form factor. The orbital contribution is therefore almost entirely quenched. (b) Spin-state density analysis. The calculated total (spin-up minus spin-down) state density as a function of energy in $CeFe_2$. Also shown are the *integrated* local spin-state densities for Ce and Fe. The Fermi energy is at zero.

tion parallel to the spin. However, our calculated $4f$ moment antiparallel to the $3d$ moment in $CeFe_2$ is actually an anomaly in a light rare earth where localized $4f$ electrons normally have a larger orbital component of the moment antiparallel to the spin component, resulting in a total moment parallel to the $3d$ moment. The anomaly is due to the quenching of the orbital $4f$ moment by band formation and is a definitive prediction of the present theory.

The calculated form factors of the magnetization density at the Fe and Ce sites are shown in Fig. 3. The Fe form factor is normal. We have plotted the form factor

for localized $4f$ states[23] for comparison, from which it is obvious that our calculated Ce form factor is anomalous since itinerancy has almost totally quenched the orbital $4f$ moment, even when spin-orbit coupling is included in the calculation. Therefore the Ce $4f$ electrons have acquired another property that is normally associated with itinerant $3d$ electrons, and it is measurable.

The spin (spin-up minus spin-down) state density, and the integrated Fe and Ce spin-state densities, are also plotted in Fig. 3. At higher binding energies the Fe spin-state density dominates but both the Fe and total spin-state densities reverse sign close to the Fermi energy where the Ce and Fe polarizations are actually *parallel*. The observation of this spin reversal in a spin-polarized photoemission experiment would be an excellent test of the present theory.

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