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α-γ transition in Ce from temperature-dependent band-structure calculations

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Temperature-dependent band-structure calculations are done for fcc Ce at different volumes. Large temperature and volume variations of the density of states, the bulk modulus, and the magnetic moments are found to give a qualitative description, within the density functional theory, of the Ce α-γ phase transition and the thermodynamic properties of the γ phase. [S0163-1829(96)06347-3]

The face-centered-cubic (fcc) phases α and γ of cerium have been studied extensively in recent years. The unusual property is the transition from the large volume γ-Ce to the low (-17%) volume α-Ce, while the two phases remain fcc.[1] At zero pressure, the α-γ transition begins at 200 K (where a hexagonal phase β comes in between), and ends in a critical point at about 570 K and 20 kB. The α phase is nonmagnetic (NM), while the larger volume γ phase is magnetic with a disordered local moment.

The nature of the f electron is a key property for an understanding of Ce but there are conflicting theories about its role. Large localization is inferred from neutron scattering,[2,3] whereas bandlike behavior appears from Compton profiles.[4] Several models explaining the unusual α-γ transition have been proposed such as the promotional model (PM),[5] the Kondo volume-collapse (KVC) model,[6] and the Mott transition (MT) model.[7] In the PM the f electron is promoted into the $5d$ conduction band at the transition volume. Density functional (DF) band calculations,[8,9] based on the local density approximation (LDA),[10] have not been able to confirm the PM. In the KVC model[6] the $4f$ electrons are assumed to be localized in both α-Ce and γ-Ce. The screening is assumed to be different in the two phases, and energies and entropies due to spin fluctuations cause the α-γ transition. The MT model[7] considers the f states to be itinerant and bonding for α-Ce, but localized, nonbonding for γ-Ce. Two similar approaches treated γ-Ce by self-interaction corrected (SIC) LDA calculations, while the low volume nonmagnetic α phase was treated within ordinary LDA.[11] An extension of the Mott picture kept one $4f$-electron frozen in an atomic corelike state for γ-Ce, but otherwise DF calculations were carried out.[12] A phase diagram was obtained assuming that the two phases are mixed as in an alloy[12] with an important magnetic entropy contribution to the free energy of γ-Ce.

In the present work we extend previous DF studies by introducing explicit T dependence in self-consistent band-structure calculations of the electronic total energy E_{tot} and entropy S_{el}.[13] A localized nature of the f electrons enters within DF theory via spin polarization in ferromagnetic (FM) and antiferromagnetic (AF) configurations, but no further modeling is done. From the magnetic spin moments (m) we estimate the entropy S_{mag} due to magnetic disorder. In addition, we estimate the vibrational free energy F_{vib} from the calculated bulk modulus.[13]

Electron energies are calculated by the linear muffin-tin orbital (LMTO) method. Our basis set includes semirelativistic s, p, d, and f valence states. The Ce-$5p$ state is included as a valence state. A number of results at $T=0$ are improved by using the generalized gradient approximated (GGA) potential[14] instead of LDA.[15] The GGA values for the equilibrium Wigner-Seitz radius (r_{WS}) 3.52 a.u. agree reasonably with experiment, 3.54 a.u. Our calculated bulk modulus ($B_0=0.51$ Mb) at this volume and at $T=0$ is somewhat larger than the experimental value (0.3 Mb). The LDA values are 3.41 a.u. and 0.60 Mb, respectively. Some variations of the moment and equilibrium volume have been found in full potential calculations.[16] However, since these variations are comparable with the variations using different potentials and since different potentials give the same qualitative results for the phase transition, it is not expected that full potential calculations are crucial here. As shown later, also variations with T and linearization energy are important for quantitative results but not essential for the mechanism. Our LDA results agree well with Ref. 9 and the transition is also found using LDA, but here we present mainly results based on GGA. No T variations of the LDA or GGA potentials are attempted.

The electronic contribution to the Gibbs energy $G_{\mathrm{el}}=E_{\mathrm{el}}+PV-TS_{\mathrm{el}}$ from single-particle electron excitations is obtained in self-consistent band calculations which include T-dependent occupation of the electron density of states (DOS) $N(\epsilon)$. The electronic entropy contributions $TS_{\mathrm{el}}=-T\int N(E)[f\ln f+(1-f)\ln(1-f)]dE$, where f is the Fermi-Dirac function and N is the density of state, of the NM, FM, and AF (very similar to FM) phases of fcc Ce are shown as a function of r_{WS} in Fig. 1 for $T=790$ and 1260 K. This term grows rapidly towards larger volumes for a fixed T. The entropy is roughly proportional to the DOS at the

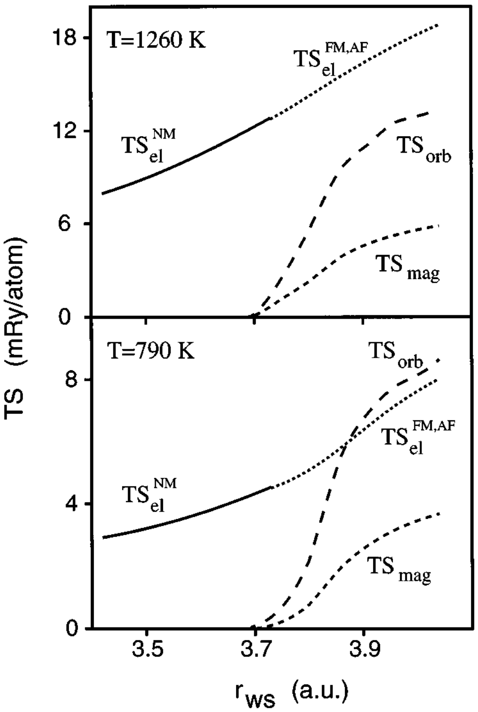

FIG. 1. Nonmagnetic (solid line) and spin-polarized (dotted line) electronic entropy contribution $TS_{\rm el}$ and magnetic disorder entropy terms $TS_{\rm mag}$ for spin only (short-dashed line) and $TS_{\rm orb}$ when including an orbital contribution (long-dashed line) versus the Wigner-Seitz radius $r_{\rm WS}$ at two temperatures, 790 and 1260 K.

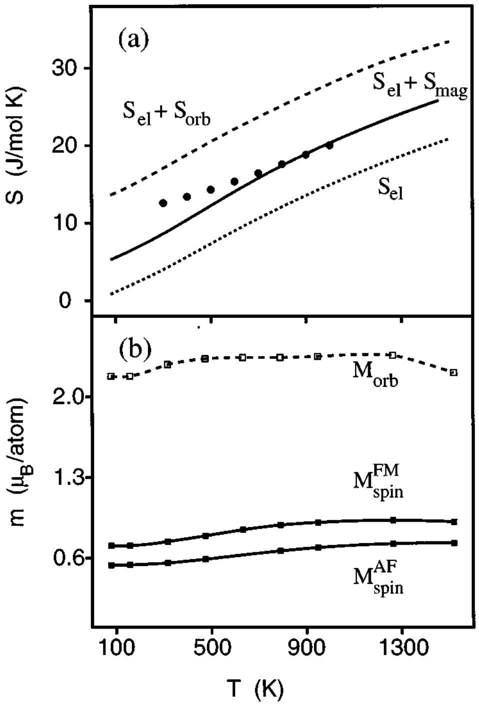

FIG. 2. (a) Calculated entropies vs temperature at $r_{\rm WS}=$ 3.96 a.u. (i.e., γ-Ce), given as $S_{\rm el}$ (dotted line), as $S_{\rm el}+S_{\rm mag}$ with spin contribution only (solid line), and as $S_{\rm el}+S_{\rm orb}$ (dashed line) when including an orbital contribution, to be compared with the experimental $S_{\rm tot}-S_{\rm vib}$ (filled circles) (Refs. 22,23). These results refer to FM configurations. (b) Temperature dependence of the spin moments of the AF and FM (solid lines) states and orbital moments (broken line) of FM fcc Ce at $r_{\rm WS}$=3.96 a.u.

Fermi energy E_F, $N(E_F)$. Since $N(E_F)$ is larger for large volumes when the bands are narrower, it makes the term $TS_{\rm el}$ important for a stabilization of Ce at larger volumes.

For each pressure and temperature, the pressure-volume relations are obtained by a Murnagon fit[17] to the *ab initio* points, from which other thermodynamic functions are derived. The bulk modulus B is then fitted to $B(V)=B_0(V_0/V)^{B_0'}$, for NM solutions. B_0, the bulk modulus at the calculated equilibrium volume V_0 for the α phase, decreases further as V is increased, because of the large pressure derivative ($B_0'=4.8$).

A simple relation between the phonon frequencies and the bulk modulus has been shown to give a good scaling relation for the Debye temperature Θ_D.[18] This procedure should be reliable here, since the scaling factor is likely to be the same for the two fcc structures. Further, our free energy difference only depends on the ratios of different Θ_D, so the absolute value of Θ_D (or B) is less important for our arguments. Due to low B, Θ_D is also very low (about 148 K at the GGA minimum of α-Ce). For temperatures larger than Θ_D we use the high-T expansion for the vibrational free energy $F_{\rm vib}=E_{\rm vib}-TS_{\rm vib}$.[19] Then the difference in vibrational free energy between the fcc phases at volumes V and V_0 is

$$\Delta F_{\rm vib}(V)=3k_BT\,\ln\left(\frac{\Theta(V)}{\Theta_0}\right)=\tfrac{3}{2}k_BT(B_0'-\tfrac{1}{3})\ln\left(\frac{V_0}{V}\right). \tag{1}$$

When $\Delta F_{\rm vib}$ is added to the electronic free energy of the FM phase, it lowers the free-energy curves for $V>V_0$, because of the lower bulk modulus. Here B is calculated from the second volume derivative of $F_{\rm el}$ for low T. This procedure is numerically stable and sufficient for a good description of the $\alpha-\gamma$ transition (see below). However, a somewhat different $B(T,V)$ ($\leqslant 10\%$) is obtained using $F_{\rm el}$ at large T. This can modify $F_{\rm vib}$ and some quantitative features of the phase transition.

The magnetic states become stable for $r_{\rm WS}>3.75$ a.u. An unusual property is that the moment increases with increasing T, see Fig. 2(b). This can be understood as a DOS effect. The DOS is very high within the f band just above E_F, and the Fermi-Dirac function probes effectively a higher $N(E_F)$ at larger T, which in turn increases the Stoner factor. Calculations for AF configurations give somewhat lower m than for the FM solutions, but the total energy is not much affected (within $1-3$ mRy/atom) and the moments increase with T. The nearly degenerate total energies for FM and AF configurations give a qualitative argument for spin disorder at larger T, since the system can change from one configuration to the other. An extension of the entropy of moments in free atoms, to the case of solids, would give $S_{\rm mag}=k_B\ln(m+1)$ per atom, for complete disorder of the spins. Further, when the spin moment is in addition to an orbital moment of a localized f level, Hund's rule gives $J=5/2$. We define a combined magnetic entropy $S_{\rm orb}=k_B\ln[2(L-S)+1]$, which includes the orbital moment (L) and a spin part $S=m/2$. By using a constant $L=3$ from

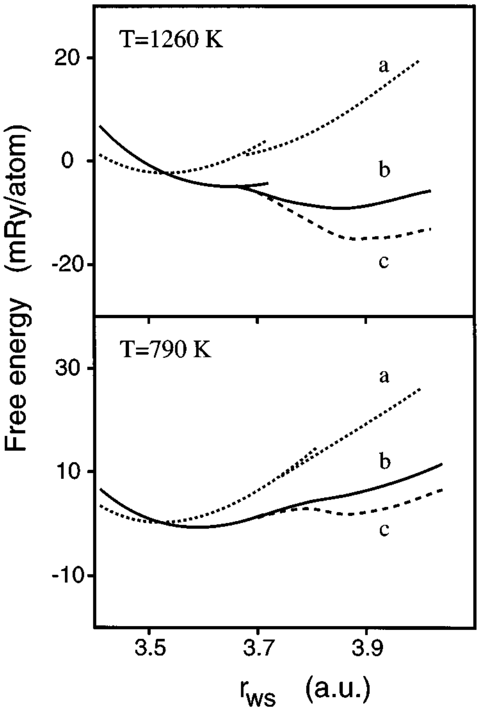

FIG. 3. (a) Electronic free energies F_{el} for NM and FM Ce, (b) corresponding $F_{el}+\Delta F_{vib}-TS_{mag}$, and (c) $F_{el}+\Delta F_{vib}-TS_{orb}$, (see text) as a function of r_{WS} at $T=790$ K and 1260 K. The zero energy is at the minimum of F_{el} for α-Ce at $T=0$ K. A transition from a low-volume phase (α) to a high volume phase (γ) is possible between the two local minima of the free energy curves.

Hund's rule in the calculation of the entropy as soon as a spin moment appears above $r_{WS}=3.75$, one finds a strong stabilizing contribution to the free energy already at rather low T. However, the minimum of the total energy is not smooth, but S_{orb} suddenly appears when $L=3$ is turned on. An approximated nonconstant value of the orbital moment can be invoked following Brooks and Kelly,[20] if the spin-orbit coupling ξ is introduced as a weak perturbation after self-consistency. Here we use such a procedure for the f band only and take ξ as a constant, 30 mRy.[21] This gradually increases L as m grows. For the largest volumes, when m saturates around 1.1 at large T, L also saturates around 3.0 as from Hund's rule. $L\sim1.9$ for $m\sim0.8$ and $L\sim0.7$ for $m\sim0.3$. Using a varying L in the calculation of the free energy gives a smooth minimum near $r_{WS}=3.9$ as seen in Fig. 3, where m is 0.7 and L is 1.8. This compares reasonably with the observation of an effective moment $\approx 2.4\mu_B$ in γ-Ce.[2]

Figure 3 shows the total free energy as function of r_{WS} at two temperatures, with and without the contributions from disordered spin and orbital moments. Without any magnetic contribution (curves a) the minimum free energy is obtained near r_{WS}=3.5–3.6 a.u., i.e., for α-Ce. If S_{mag} is added (curves b) a second minimum appears at high T near r_{WS}=3.9 a.u., i.e., for γ-Ce. At $T\approx$ 1300 K, γ-Ce has the lowest free energy and thus is stabilized at a transition temperature T_s near 1100 K. If finally S_{mag} is replaced by S_{orb} (curves c), the α-γ transition temperature T_s appears even nearer to 800 K. This is to be compared with the experimental T_s of 200−300 K at low pressure. In LDA we get $T_s\approx1500$ K when only S_{mag} is considered.

We now compare our *ab initio* results with experimental information on the entropy. The phonon spectrum in γ-Ce at 295 K has been measured by neutron scattering.[22] From the phonon density of states $F(\omega)$ we accurately get a vibrational entropy S_{vib} at any T, using $F(\omega)$ at 295 K. To this term one should add a correction due to anharmonicity when $T>$ 295 K. Lacking detailed information on the anharmonicity we instead analyze $S_{tot}-S_{vib}$ where S_{tot} is the recommended experimental entropy.[23,24] $S_{tot}-S_{vib}$ has contributions from one-electron excitations S_{el} and magnetic disorder S_{mag} (or S_{orb}). In the simplest model description S_{el} is linear in T, while S_{mag} (and S_{orb}) is constant. However, as is seen in Fig. 2, our calculated S_{el} is not exactly linear in T (due to the T dependence through the DOS). Further, it was noticed above that m varies with T.

We first focus on $S_{tot}-S_{vib}$ at room temperature, which is accurately known from experiments. It is seen from Fig. 2 (a) that although S_{el} contributes an essential part of $S_{tot}-S_{vib}$, agreement with experiment requires a magnetic entropy which is between those calculated with and without orbital moments. A reduction of the entropy S_{orb} with fully developed orbital moments might arise from partial correlation between the moments on neighboring atoms. Thus, an important orbital term in addition to the spin term is essential for an understanding of entropy data. The trends in our calculated entropies at high T are in reasonable agreement with experiment, Fig. 2 (a), but the experiments and also the description of the electronic structure including magnetic moments become less reliable at very high T.

Orbital moments are not incompatible with DF results, although their amplitudes have been determined only approximately here. What is important is the fact that the thermodynamic conditions can be described entirely by DF results provided that all entropies are considered. It should be noted that the $\alpha-\gamma$ transition appears even when only S_{mag} is considered, both in LDA and GGA, but a more realistic T_s is found when the orbital moment is also included. The electronic entropy and vibrational free energies both contribute to a large thermal expansion of α-Ce, while the onset of magnetic states and their magnetic entropies stabilize the γ phase at a large T and V. The f band is very narrow and some sensitivity to the choice of linearization energy is noticed. This should not change the conclusion concerning the reasons for the α-γ transition, but nonlinear band methods may make a difference for quantitative results. The band results show no dramatic localization at the transition, but the calculated spin density is localized for γ-Ce since it is due to the f electrons. The magnetic form factor is extended, especially for the AF cases.

In conclusion we find a consistent picture of the α-γ transition in Ce, where both phases are described as itinerant band solids. The stabilization of the high volume γ phase is due to a combination of electronic, vibrational, and magnetic entropies. The latter part may be treated by disordered spin moments only, in order to rely exclusively on *ab initio* calculations. But by including approximate orbital moments, we obtain more realistic transition temperatures and a good description of the entropy. These DF results do not have difficulty in reconciling large differences in total energy between α- and γ-Ce that arise in calculations with restricted f occupation.[9,12] It is also noted that no phase mixing is needed. These results are in contrast to the picture of γ-Ce as a system which is too localized to be described within DF theory. Although the localized picture is widely accepted, our results show that the case is still not settled and more work is required.

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