Thermodynamics of the $\alpha$-$\gamma$ transition in cerium studied by an LDA + Gutzwiller method

Ming-Feng Tian,$^{1,2,3}$ Hai-Feng Song,$^{1,3}$ Hai-Feng Liu,$^{1,3}$ Cong Wang,$^1$ Zhong Fang,$^2$ and Xi Dai$^2$

$^1$Data Center for High Energy Density Physics, Institute of Applied Physics and Computational Mathematics, Beijing 100088, China
$^2$Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
$^3$Software Center for High Performance Numerical Simulation, China Academy of Engineering Physics, Beijing 100088, China

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The $\alpha$ to $\gamma$ transition of the cerium metal has been studied in both zero and finite temperature by Gutzwiller density functional theory. We find that the first order transition between $\alpha$ and $\gamma$ phases persists to the zero temperature with negative pressure. By further including the entropy contributed by both electronic quasi-particles and lattice vibration, we also obtain the total free energy at given volume and temperature, from which we obtain the $\alpha$ to $\gamma$ transition from the first principle calculation.

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Once a material contains $f$-electrons sitting on the brink of itineracy to localization transition, its lattice and electronic degree of freedom will be strongly coupled to each other leading to fascinating structural phase diagrams. The most famous examples are the structural phase transitions with large volume changes in metal plutonium and cerium. Comparing with the situation of plutonium, the cerium metal is much simpler because it has only one $4f$ electron, which makes it an "prototype material" to study the structural phase transitions in $f$ electron materials.

Among the phase transitions in cerium metal, enormous research interests have been attracted to the $\alpha$ to $\gamma$ transition, which is an iso-structural transition with volume collapse as large as 14% at room temperature and pressure around 0.8 GPa [1, 3]. The transition pressure rises with increasing temperature, and seems to end at a solid-solid critical point (CP) around $P_c = 1.5$ GPa and $T_c$ slightly under 500 K [2, 5]. The nature of this transition has still under debate and become one of the classical problems in condensed matter physics.

The key issues under debating can be summarized into the following three aspects. i) Although it is commonly believed that the electronic states of $4f$ orbitals undergo a dramatic change from $\alpha$ to $\gamma$ phases, whether this change can be better described by Mott transition model [1, 2] or Kondo volume collapse (KVC) model [7–9] is still under debating [2, 11–12]. The main difference between the above two models is the role of the spd bands. In Mott transition model, these spd bands are nearly "spectators" of the transition and the $4f$ bands become completely localized in the $\gamma$ phase. While in the view point of KVC, there are no qualitative difference between $\alpha$ and $\gamma$ phases. The only difference is the scale of Kondo temperature. ii) Since the $\alpha$ to $\gamma$ transition also happens at finite temperature with ambient pressure, it is quite clear that entropy difference is one of the important driving force for the transition. The question is whether the transition is purely driven by entropy? In another words, whether or not such a transition can also be induced at the zero temperature (for example by negative pressure), where entropy plays no role. iii) Given the fact that entropy is important to the transition, what is its origin? Is it mainly contributed by electronic entropy or lattice entropy?

Besides the experimental studies [2, 11–16], the first principle calculation is another powerful tool with parameter free to study the nature of the structural phase transitions. In the density-functional theory (DFT) calculations with local density approximation (LDA) or general gradient approximation (GGA), the correlation effects among the $f$ electrons have not been fully considered in a satisfactory way, leading to overestimation of the kinetic energy for the $f$ electrons. Therefore as one of the consequences, only the $\alpha$ phase of cerium can be obtained and there is no signal for the appearance of $\gamma$ phase at all even after including both the electronic and vibrational entropy [17–20]. While on the other hand, the self-interaction corrected local spin density approximation (LSDA) [19, 21, 22] and LSDA + U calculations can obtain the $\gamma$ phase by assuming the $4f$ electrons to be either completely localized or magnetic, but still it is difficult for these methods to describe both phases under a unified physical picture. Besides, a calculation base on hybrid density functionals obtain two distinct solutions at zero temperature that can be associated with the $\alpha$ and $\gamma$ phases of Ce [23], but the results have not yet extended to the finite temperature case. Nevertheless, a recent work from density functional theory proposed that thermal disorder contributes via entropy to the stabilization of the $\gamma$ phase at high temperature [24], the $\alpha$-$\gamma$ transition is calculated to occur around 600 K.
Within the LDA + DMFT method, a combination of LDA with dynamical mean field theory (DMFT), early numerical studies have been carried out to study the phase transitions of Ce at finite temperature \[^{22}^{31}\]. While since the quantum Monte Carlo methods have been adopted as the impurity solver of DMFT, it is difficult for LDA + DMFT to study the transition in low temperature and the full thermodynamic features of the transition in the full temperature range have yet to be obtained.

In this letter we show that LDA + Gutzwiller method, which incorporate LDA with Gutzwiller variational approach, can be well applied to study the ground properties of the cerium metal and with the generalization to the finite temperature, it can be further applied to study the thermodynamic properties of the \(\alpha\) to \(\gamma\) transition in low temperature. Here we will sketch the most important aspects of the method, and leave the details to Refs. \[^{32}^{34}\]. The total Hamiltonian to describe the strongly correlated systems can be written as

\[
H = H_{LDA} + H_{int} - H_{DC},
\]

where \(H_{LDA}\) is the single particle Hamiltonian obtained by LDA and \(H_{int}\) is the local interaction term for the \(4f\) electrons. \(H_{DC}\) is the double counting term representing the interaction energy already considered at the LDA level. In the present letter, we compute the double counting energy using the scheme described in Ref. \[^{33}\]. In LDA + Gutzwiller we apply the following Gutzwiller trial wave function, \(|G\rangle = P_G|0\rangle\), where \(P_G\) is the Gutzwiller projectors containing variational parameters to be optimized by the variational principle and the non-interacting state \(|0\rangle\) is the solution of the effective Hamiltonian for the quasi-particles \(H_{eff} \approx P_G H_{LDA} P_G\).

The ground state properties of cerium metal have been studied using LDA + Gutzwiller by us for the positive pressure case \[^{35}\] and recently by G. Kotliar’s group for the negative pressure case \[^{34}\], where they find that for interaction strength \(U < 5.5eV\) the first order transition between \(\alpha\) and \(\gamma\) phases survives at zero temperature, they also reported a new implementation of the Gutzwiller approximation \[^{37}^{39}\].

In the present letter, we apply the LDA + Gutzwiller method implemented in our pseudo potential plane wave code BSTATE \[^{32}^{33}^{35}^{40}\] to obtain the ground state energy of cerium metal crystallized in face centered cubic (fcc) structure. The LDA part of the calculations were performed with the full consideration of the relativistic effect and a \(16\times16\times16\) k mesh for higher energy converged precision.

Our main results in zero temperature are shown in Fig. (1a). The negative curvature region in the total energy versus volume curve, which signals the first order transition with pressure, is present for all interaction strength, which is slightly different with the results obtained by G. Kotliar’s group \[^{34}\]. With interaction strength \(U = 4.0eV\), both the experimental volume \((28.0 - 29.0\;\text{Å}^3)\) and bulk modulus \((20.0 - 35.0\;\text{GPa})\) \[^{31}^{33}^{35}\] at ambient pressure can be nicely reproduced and we will adopt this value for the calculations through out the paper. The quasi-particle weight and the average occupation of both the \(j = 5/2\) and \(7/2\) bands are plotted in Fig. (1c) and (d). From Fig. (1d) one can find that the occupation number of \(j = 5/2\) bands increase dramatically from 0.7 to almost one in the volume regime from 29.0 \(\text{Å}^3\) (the equilibrium volume of the \(\alpha\) phase) to 35.0\(\text{Å}^3\) (the equilibrium volume of the \(\gamma\) phase) and at the same time the quasi-particle weight drops abruptly (Fig. (1c)), indicating that the \(f\)-electrons is quite itinerant in \(\alpha\) phase while becomes quite localized in \(\gamma\) phase, which can be better described by the Kondo lattice model.

In order to directly compare the first principle results with the experimental data, which is always performed at finite temperature, the calculations of the free energy at finite temperature is strongly desired. In the present letter, we generalize the LDA + Gutzwiller method to calculate the free energy by including both the electronic and lattice vibrational entropy. The total Helmholtz free energy can be always written as

\[
F(V, T) = F_{el}(V, T) + F_{lat}(V, T)
\]

where \(F_{el}(V, T)\) and \(F_{lat}(V, T)\) are the electronic and lattice vibrational part of the free energy respectively. In the present study, we assume that at least in the low temperature both the \(\alpha\) and \(\gamma\) phases are in the fermi liquid

\[
F(V, T) = F_{el}(V, T) + F_{lat}(V, T)
\]
region, where the electronic entropy can be calculated by counting the thermally excited quasi-particles. Near the critical temperature, which is around 500K, the $\gamma$ phase will be no longer in the fermi liquid phase any more, leading to possible underestimation of the electronic entropy in $\gamma$ phase, which will be discussed in more detail below.

Therefore in the present study, the electronic free energy will be estimated as

$$F_{el}(V, T) = \int n_{qp}(\epsilon, V) f(\epsilon) d\epsilon$$

$$T k_B \int n_{qp}(\epsilon, V) \left[ f \ln f + (1 - f) \ln (1 - f) \right] d\epsilon$$

where $n_{qp}(\epsilon, V)$ is the quasi-particle density of states obtained by solving the Gutzwiller effective Hamiltonian $H_{eff}$ and $f(\epsilon)$ denotes the Fermi-Dirac distribution function. The first and second terms in the above equation denote the energy and entropy contributions to the electronic free energy respectively.

The lattice part of the free energy is estimated within the mean field approximation proposed in the references [18, 44, 45], where the vibrating motion of the cerium atoms can be approximately treated as independent three dimensional oscillators moving under the harmonic potential formed by all the surrounding atoms. The strength of such mean field potential can be approximately determined by the curvature of the total energy versus volume curve as explained in detail in reference [18, 44, 45]. Considering the heavy mass of the cerium atoms, we can further treat the atomic motion classically and get the lattice free energy as

$$F_{lat}(V, T) = -k_B T \left( \frac{3}{2} \frac{1}{\pi \hbar^2} \right) m k_B T + \ln \nu_f(V, T)$$

where

$$\nu_f(V, T) = \frac{3}{2} \pi \int \exp(-\frac{g(r, V)}{k_B T}) r^2 dr$$

$$g(r, V) = \frac{1}{2} [E_c(R + r) + E_c(R - r) - 2 E_c(R)]$$

where $r$ represents the distance that the lattice ion deviates from its equilibrium position, $R$ is the lattice constant, and $V = R^3/4$ in the case of fcc crystal.

The free energy curves with different temperature in Fig. 2(b) reveals the competition between the $\alpha$ and $\gamma$ phases, the free energy difference between $\gamma$ phase and $\alpha$ phase decreased with increasing temperature, which becomes almost zero at a temperature of 190 K. This results illustrate that the $\alpha$-$\gamma$ transition temperature is 190 K at zero pressure, which agrees well with the experimental data.

The pressure at given volume and temperature can be estimated as $P(V, T) = -\partial F(V, T) / \partial V$, we calculate the pressure versus volume isotherms of fcc Ce, as shown in Fig. 2. At given pressure, the first order phase transition can be signaled by the appearance of multiple solutions with different volumes, which has been plotted in the figure by the open symbols indicating the region of thermodynamic instability.

The calculated phase diagram has been plotted in Fig. 3 together with the comparison to the experimental data from several different papers. The agreement between our LDA + Gutzwiller calculation and experimental data is surprisingly well.

Whether the $\alpha$ to $\gamma$ transition is mainly driven by entropy is another key question. In this letter, we try to address it by comparing the change of three parts of Gibbs free energy upon the transition, $T \Delta S$, $P \Delta V$ and internal energy $\Delta E$, which are plotted in Fig. 4(b) together with the experimental results in Fig. 4(a) taken from reference (13, 47, 48). Our results show that the biggest contribution to the transition comes from the entropy change which is quite consistent with the experimental data (13, 47, 48). We can further separate the entropy contribution into electronic and lattice parts, which is also illustrated in Fig. 4(b). The electronic entropy change obtained by our LDA + Gutzwiller calculation is about 5.0 meV/atom, which is about 2-3 times smaller than the lattice part. This is mainly due to the fact that in LDA + Gutzwiller only the quasi-particle entropy has been included but not the magnetic entropy coming from the incoherent motion of the $f$-electrons. Considering the estimated Kondo temperature for $\gamma$ phase is about 70 K (12), the magnetic entropy, may also make sizable contri-
In conclusion, the thermodynamic features of the cerium $\alpha$ to $\gamma$ transition has been obtained by applying the LDA + Gutzwiller method. Our calculations show that the long puzzled transition is actually mainly driven by the entropy change, where both the electronic and the lattice part play important roles.

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FIG. 3: (Color online) Pressure vs temperature phase diagram of fcc Ce. Open and close circles denote present LDA + G data. The other symbols are previous experimental data ($\Diamond$, $\triangle$, $\square$, $\nabla$, $\star$).

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FIG. 4: (Color online) Energy related term across the $\alpha$-$\gamma$ transition, upper panel is experiment ($\Diamond$, $\square$, $\triangle$, $\nabla$, $\star$), lower panel is present data ($\Delta$ electronic entropy, $\nabla$ entropy of phonon). Entropy term $T\Delta S$ (solid symbols), $P\Delta V$ (open symbols), and internal energy $\Delta E$ (open symbols overlaps with plus).
[22] A. Svane, Phys. Rev. Lett. 72, 1248 (1994).
[23] M. Casadei, X. Ren, P. Rinke, A. Rubio, and M. Scheffler, Phys. Rev. Lett. 109, 146402 (2012).
[24] T. Jarlborg, Phys. Rev. B 89, 184426 (2014).
[25] M. B. Zöll, I. A. Nekrasov, T. Pruschke, V. I. Anisimov, and J. Keller, Phys. Rev. Lett. 87, 276403 (2001).
[26] K. Held, A. K. McMahan, and R. T. Scalettar, Phys. Rev. Lett. 87, 276404 (2001).
[27] A. K. McMahan, K. Held, and R. T. Scalettar, Phys. Rev. B 67, 075108 (2003).
[28] K. Haule, V. Oudovenko, S. Y. Savrasov, and G. Kotliar, Phys. Rev. Lett. 94, 036401 (2005).
[29] A. K. McMahan, Phys. Rev. B 72, 115125 (2005).
[30] B. Amadon, S. Biermann, A. Georges, and F. Aryasetiawan, Phys. Rev. Lett. 96, 066402 (2006).
[31] B. Chakrabarti, M. E. Pezzoli, G. Sordi, K. Haule, and G. Kotliar, Phys. Rev. B 89, 125113 (2014).
[32] X. Deng, X. Dai, and Z. Fang, Eur. Phys. Lett. 83, 37008 (2008).
[33] X. Y. Deng, L. Wang, X. Dai, and Z. Fang, Phys. Rev. B 79, 075114 (2009).
[34] K. M. Ho, J. Schmalian, and C. Z. Wang, Phys. Rev. B 77, 073101 (2008).
[35] M.-F. Tian, X. Deng, Z. Fang, and X. Dai, Phys. Rev. B 84, 205124 (2011).
[36] N. Lanatá, Y.-X. Yao, C.-Z. Wang, K.-M. Ho, J. Schmalian, K. Haule, and G. Kotliar, Phys. Rev. Lett. 111, 196801 (2013).
[37] N. Lanatá, H. U. R. Strand, Y. Yao, and G. Kotliar, Phys. Rev. Lett. 113, 036402 (2014).
[38] N. Lanatá, Y. Yao, C.-Z. Wang, K.-M. Ho, and G. Kotliar, arXiv p. 1405.6934 (2014).
[39] N. Lanatá, Y.-X. Yao, C.-Z. Wang, K.-M. Ho, and G. Kotliar, arXiv p. 1407.4862 (2014).
[40] G. T. Wang, X. Dai, and Z. Fang, Phys. Rev. Lett. 101, 066403 (2008).
[41] F. H. Ellinger and W. H. Zachariasen, Phys. Rev. Lett. 32, 773 (1974).
[42] W. H. Zachariasen and F. H. Ellinger, Acta Cryst. A33, 155 (1977).
[43] J. S. Olsen, L. Gerward, U. Benedict, and J. P. Itié, Physica B 133, 129 (1985).
[44] E. Wasserman, L. Stixrude, and R. E. Cohen, Phys. Rev. B 53, 8296 (1996).
[45] H.-F. Song and H.-F. Liu, Phys. Rev. B 75, 245126 (2007).
[46] K. A. Gschneidner, Valence instabilities and related narrow band phenomena (Plenum, New York, 1977), p. 89.
[47] A. Schiwek, F. Porsch, and W. B. Hopzapfel, High Press. Res. 22, 407 (2002).