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Crystal fields and the $\gamma \rightarrow \alpha$ transition in Ce

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Abstract

In the $\gamma \rightarrow \alpha$ transition of Ce, the material undergoes an isostructural change at which the volume changes by 15% and the magnetic character changes. Recently, the transition has been described in terms of a balance between the free-energy of the magnetic moments and the characteristic energy scale of the α phase. The field-temperature dependence of the phase diagram has been predicted, and was confirmed by experiment. Inelastic neutron scattering experiments on the γ phase of Ce have shown indications of crystal field splittings, and similar experiments have determined the energy scale of the α phase. We shall examine the effects of the crystalline field splittings within the framework of NCA calculations on the single-impurity Anderson model, and examine their consequence for the phase diagram.

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Keywords: $\alpha \rightarrow \gamma$ Phases of Ce; Crystal field levels

The $\gamma \rightarrow \alpha$ transition in Ce has been the subject of much investigation since the 1940s. The transition between the high-temperature γ phase and the low-temperature α phase is isostructural and is manifested by a large decrease in volume($\sim$17%) [1]. In the high-temperature γ phase, the magnetic susceptibility follows a Curie–Weiss temperature dependence, but in the low-temperature α phase, the susceptibility is suppressed and follows a Pauli–paramagnetic temperature dependence, with a characteristic energy which was later found to be as large as 165 meV [2]. Pauling [3] and Zachariasen suggested that the f electrons are squeezed into the valence band in the transition. The Pauling–Zachariasen model was challenged when Gustafson and co-workers [4] performed positron annihilation measurements which indicated that there was no significant change in the number of f electrons. Subsequently, Johansson [5] suggested that the transition was a Mott transition in which the localized magnetic 4f electron states were transformed into a broad non-magnetic 4f band of Bloch states. However, photoemission experiments contradict a simplified picture of the Mott transition. Allen and Martin then suggested that the phase transition was due to a Kondo volume collapse [6]. In this picture, the transition is due to the competition between the entropy of the six-fold degenerate magnetic ion in the high-temperature state and the binding energy of a Kondo singlet ($\sim k_B T_K$) formed in the low-temperature state. This requires that the electronic entropy change, per Ce ion, should be of the order of $k_B \ln 6 \sim 1.79\, k_B$, which is similar to the total entropy change of $1.54\, k_B$ inferred from the latent heat. However, at high pressure, measurements of the Debye–Waller factor indicate that roughly $0.75\, k_B$ of the total entropy change is associated with phonons [7]. These measurements and the results of our present NCA calculations, which yield an electronic entropy change of only about $1.1\, k_B$, suggest that the lattice must play an important role in the transition. In fact, the lattice energy, along with the local correlation energy, has been calculated within the local-density-functional dynamical-meanfield approximation [8]. These calculations are promising as they show features consistent with the existence of the observed critical end-point at $T_c \sim 550$ K.

We shall compare our NCA calculations including cubic crystal field splittings with the neutron scattering data on the γ phase at ambient pressures [9,10] and we shall also

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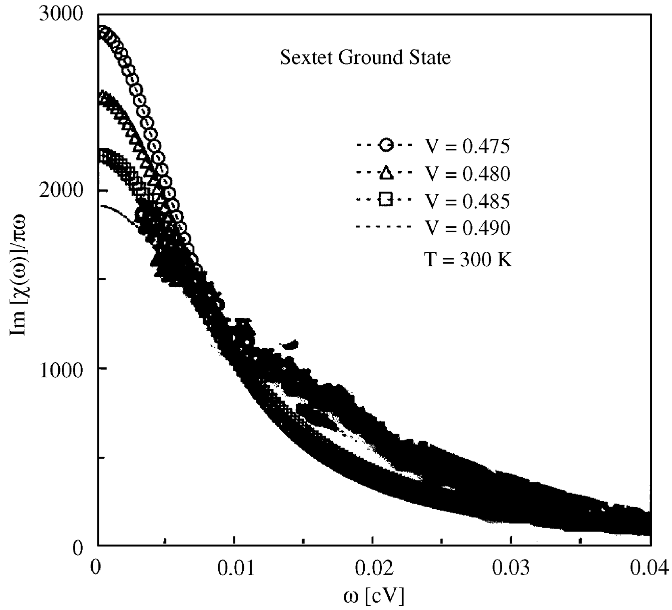

Fig. 1. A comparison of the NCA calculations with $J = \frac{5}{2}$ and no crystal field splittings and various values of the hybridization V (in eV), with the experimental data of McQueeney et al. [9].

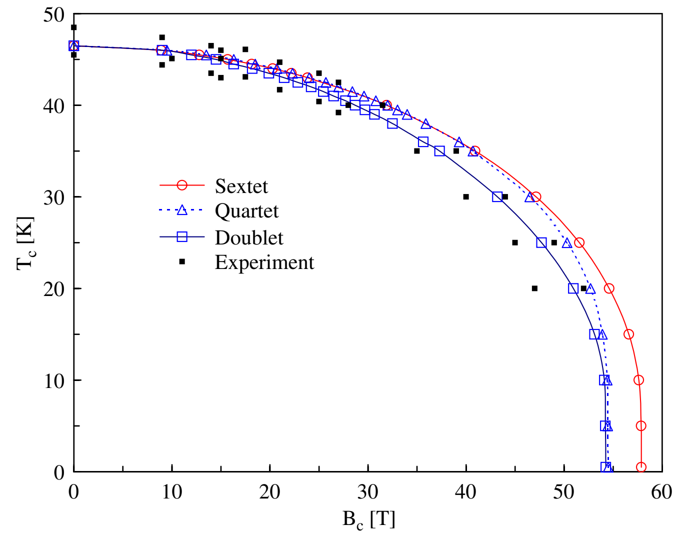

Fig. 2. The calculated phase diagram of $Ce_{0.8}La_{0.1}Th_{0.1}$ assuming cubic crystal fields with a splitting of 18 meV, no crystal field splitting and the experimental data (filled squares) [11].

with the experimentally determined phase diagram of $Ce_{0.8}La_{0.1}Th_{0.1}$ [11].

We have calculated the neutron scattering cross-section of the single impurity Anderson model using the NCA, with $J = \frac{5}{2}$ (Fig. 1). The best fit of the neutron scattering on γ Ce shows evidence of a broadened crystal field level at about 18 meV. Due to the large width of the inelastic "peak" [10], comparison of the data with calculations assuming a cubic crystal field is indecisive as to whether the crystal field quartet or the doublet has the lowest energy. The quartet ground state does produces a slightly better fit. The calculated value of the f occupation is about 0.95 for the γ phase and is 0.8 in the α phase. The value of 0.8 is consistent with a Kondo condensation energy of 165 meV [2]. Since the γ phase is dominated by the local moments which are absent in the α phase, Dzero et al. suggested that the (B, T) phase diagram should be determined by the balance of the magnetic free energy with the (field-independent) condensation of the low-temperature phase [12]. In Fig. 2, we show the effects of crystal field splitting on the observed phase diagram of $Ce_{0.8}La_{0.1}Th_{0.1}$ [11]. It is seen that the experimental data support the hypothesis of a crystal field doublet ground state. Since this is also inconclusive, we suggest that the observation of a metamagnetic transition for fields of the order of 200 T would conclusively demonstrate that the doublet is the crystal field ground state. The metamagnetic transition is predicted to be absent for a quartet crystal field ground state.

We have analyzed the results of inelastic neutron scattering in the γ phase of Ce and find evidence of (broadened) crystal field splittings. Support for the existence of these crystal field levels is provided by analysis of the phase diagram of $Ce_{0.8}La_{0.1}Th_{0.1}$. A definitive determination of the crystal field ground state may be provided by the observation of a metamagnetic transition at high fields. Our NCA calculations, with crystal field splittings, do show that a significant fraction of the entropy change in the $\gamma \rightarrow \alpha$ transition is of non-electronic origin. Therefore, we conclude that the lattice does play an important role in the transition.

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