



Optical spectroscopy and photoemission of α - and γ -cerium from LDA + DMFT

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Abstract

Using a novel approach to calculate optical properties of strongly correlated systems, we address the old question of the physical origin of the $\alpha \rightarrow \gamma$ transitions in Ce. We find that the Kondo collapse model, involving both the f and the spd electrons, describes the optical data better than a Mott transition picture involving the f electrons only. Our results compare well with existing experiments on thin films. We predict the optical spectra for both α and γ phases of Ce and find the development of a hybridization pseudogap in the vicinity of the phase transition.

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Cerium metal with a single electron in the f shell is a classic example of an electronic transition induced by temperature and/or pressure. At a temperature less than 600 K and pressure less than 20 kbars, it undergoes a transition between two isostructural phases, a high-pressure phase or α phase and a low-pressure γ phase. In α -Ce the f electron is delocalized (for example the spin susceptibility is temperature independent) while in γ -Ce the f electron is localized (for example the electron has a Curie-like susceptibility). Several

basic questions about this transition are still being debated. What is the driving mechanism of this transition? How is the electronic structure coupled to the volume changes? What is the role of the ‘heavy’ f and the ‘light’ spd electrons which are near the Fermi level in this material? These fundamental questions continue to be the subject of experimental investigations [1].

Two main theoretical hypotheses have been advanced to describe the electronic structure changes across the α - γ boundary. Johansson proposed a Mott transition scenario [2], where electrons from the f bands are itinerant and conducting in α phase while they are localized

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and insulating in γ phase. In the latter case, the f electrons do not participate in the bonding, explaining the volume collapse. In this picture, the spd electrons are mere spectators and unimportant for explaining the $\alpha \rightarrow \gamma$ transition.

A different view on this problem was proposed by Allen and Martin [3] who introduced the Kondo volume collapse model (KVC). They suggested that the transition was connected with modifications in the effective hybridization of the spd bands with the f-electron. The main change when going from α to γ is the degree of hybridization and hence the Kondo scale.

More recently, the modern dynamical mean field theory (DMFT), in combination with realistic band structure calculations (LDA+DMFT) was brought to bear on this problem [4]. LDA+DMFT allowed the computation of the photoemission spectra of cerium in both phases, and the thermodynamics of the transition starting from first principles.

Formalism: Within the LDA+DMFT method, the LDA Hamiltonian is superposed by a Hubbard-like local Coulomb interaction, which is the most important source of strong correlations in correlated materials and is not adequately treated within LDA alone. The resulting many-body problem is then treated in DMFT spirit, i.e., neglecting the nonlocal part of self-energy. The local part of self-energy can be calculated from the corresponding impurity problem, which is solved here with the one-crossing approximation [5]. The optical conductivity within DMFT is calculated from a bubble diagram only, since the two-particle vertex is local in this theory and therefore vertex corrections vanish. The details of the calculation has been given elsewhere [6].

Results: The photoemission spectra close to the Fermi level, is dominated by the f electron density of states. The optical spectroscopy, on the other hand, can probe also the conducting spd bands and, as we will show later, is very sensitive to the hybridization effects between the f's and spd's. In the top panel of Fig. 1, we present the results of our calculation for bulk cerium, while in the bottom panel, the results of recent experiment on thin films [1] are reproduced. The results of LDA calculation are also shown.

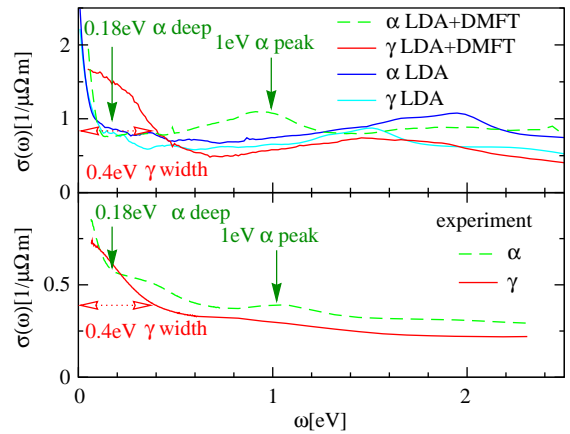


Fig. 1. Top panel shows the calculated optical conductivity for both α and γ phases of cerium. The thick lines correspond to the LDA+DMFT method and the thin lines to LDA. The temperature used in calculation is 580 K, while the volumes of the α and γ phases are 28.06 and 34.37 \AA^3 , respectively. The bottom panel shows experimental results measured by the group of D. van der Marel [1]. The measurements for α phase were done at 5 K and for γ phase at 400 K.

The optical conductivity of γ -Ce is fairly featureless, consisting of a very broad Drude-like peak of half-width 0.4 eV on a constant background. The α phase, has a much narrower Drude peak with a width of the order of 0.1 eV and a peak at 1 eV. The latter feature is remarkable because, as pointed out in Ref. [1], it indicates that when going from γ to α the electronic structure of cerium is modified on an energy scale larger than the Kondo energy. All these important qualitative features are present in both theory and experiment. Note that LDA predicts a narrow Drude peak in both phases while the 1 eV peak in the α phase is absent.

The optical conductivity is dominated by the d bands because the f velocities are orders of magnitude smaller than d velocities. In the Mott transition picture, the spd electrons are pure spectators, and hence no appreciable changes in the optical spectrum should be observed across α to γ transitions. On the other hand, if the hybridization between the spd electrons and the f electrons increases upon entering the α phase (as proposed in KVC model), we expect a hybridization pseudogap to develop as the temperature is

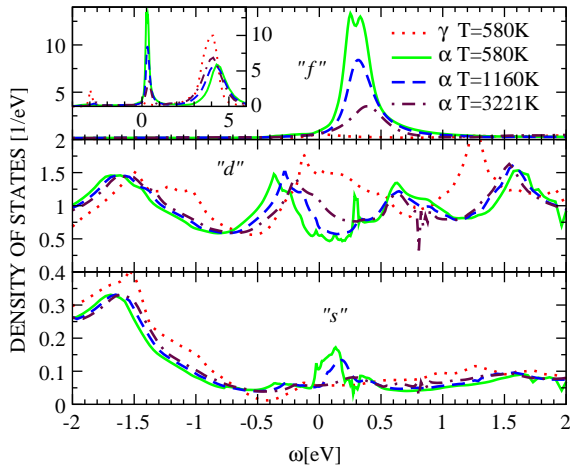


Fig. 2. Temperature dependence of partial density of states for both phases α and γ of Ce. The upper panel shows $L = 3$, the middle panel $L = 2$ and the bottom panel $L = 0$ density of states. The inset shows the f density of states in the extended frequency range, where also the upper Hubbard band is clearly visible.

lowered because spd carriers are strongly modified as they bind to the f electrons.

As one can see in Fig. 2, the d bands in α phase have a very pronounced hybridization pseudogap

which is grown by lowering the temperature, exactly as the Kondo peak builds up. The spectral weight is transferred from the Fermi level into the side-peaks which are 1 eV apart causing 1 eV peak in optical conductivity. In the γ phase, the Kondo peak disappears because the effective hybridization of the f with spd electrons is smaller and the coherence scale T_K is reduced for at least an order of magnitude. Thus, the d bands are almost decoupled from the f 's leading to a broad Drude-like peak of width 0.4 eV.

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