Electronic properties of $\delta$-Ce

Li Huang and Chang’an Chen
National Key Laboratory for Surface Physics and Chemistry, PO Box 718-35, Mianyang 621907, Sichuan, People’s Republic of China
E-mail: huangli712@yahoo.com.cn

Abstract. In order to gain a valuable insight into the essence of 4f electron in the $\delta$ phase cerium (bcc structure), full-potential linearized augmented plane wave method supplemented with GGA+$U$ correction has been employed to study its bulk, electronic, and optical properties. The present equilibrium volume and bulk modulus are in accord with the experimental values. The 4f spectrum only consists two separate Hubbard bands, and at Fermi level the spectral weight of 4f characters can be neglect. It is argued that the f electron in $\delta$ phase is highly correlated. The surprising similarity between the dielectric functions of $\delta$-Ce and $\gamma$-Ce is also addressed, which can be understood in the resemblance of degree of 4f electron correlation.

1. Introduction

Metallic cerium has unique properties compared with neighboring elements in the rare earth series [1]. It exhibits an extraordinary rich pressure-temperature phase diagram, which has inspired numerous theoretical and experimental interests. The most fascinating property of Ce metal is the occurrence of the $\gamma - \alpha$ isostructural (fcc-to-fcc) transition, which involves a volume collapse of ~16% [1]. To address this problem several hypotheses have been advanced. It is generally believed that this transition arises from changes in the degree of 4f electron correlation, as is reflected in both Mott transition (MT) [2] and Kondo volume collapse (KVC) [3–5] models. Both models agree that the $\gamma$ phase is strongly correlated. The discrepancy between the two models lies in the electronic state of 4f electron in $\alpha$-Ce. In the MT scenario, the 4f electron in $\alpha$ phase is treated to be itinerant, whereas the KVC model assumes continued strong correlation with Kondo screening by the valence electrons of the persistent 4f moments.

The electronic structures of $\alpha$ and $\gamma$-Ce have attracted many attentions, nevertheless, that of $\delta$-Ce is of less concerned. We note that the knowledge on electronic structure of $\delta$-Ce may be helpful to the elucidation of phase transitions among multiple allotropic forms and other intriguing properties of Ce. Furthermore, it also sheds light to the evolution of degree of 4f electron correlation. Unfortunately, both experimental and theoretical knowledge about the inherent properties of 4f electron in $\delta$ phase is insufficient. To our best knowledge, the electronic structure of $\delta$-Ce by first-principles approach has not been reported until now. It is therefore the aim of this contribution to supplement the missing information about the electronic properties of $\delta$-Ce.

2. Computational Details

The calculations reported in this paper have been performed using the WIEN2K package [6], which is an implementation of the density functional full-potential APW+lo method that makes
Table 1. Calculated bulk modulus (B) and equilibrium volume (V) of δ-Ce along with experimental data.

|       | GGAa | GGA+ Ua | Experimentb |
|-------|------|---------|-------------|
| V(Å³) | 26.47| 35.16   | 34.97       |
| B(GPa)| 32.55| 17.30   | 18.70       |

a The present work.  
b Reference [10].

no shape approximation to the potential or density. The APW+lo method expands the Kohn-Sham orbitals in atomic like orbitals inside the atomic spheres and plane waves in the interstitial region. The formalism of this method has been described in detail elsewhere [7]. The selected atomic sphere radii (R\text{mt}) is 2.5 a.u. A plane wave expansion described by R\text{mt}K\text{max} equals to 7 and \(k\) sampling with a 15 × 15 × 15 \(k\)-points mesh (4000 \(k\)-points in the whole Brillouin zone) turns out to be satisfactory. A number of tests have been carried out to ensure convergence with respect to different \(k\)-points meshes and cutoff energies. The calculations have been completed utilizing the generalized gradient approximation (GGA) with the potential proposed by Perdew, Burke, and Ernzerhof [8].

According to the MT scenario, the 4\textit{f} electron of γ-Ce is highly correlated [2]. But the essence of 4\textit{f} state in δ phase is presently not clear. Thus we considered it in two different perspectives, i.e., itinerant or correlated electron. The former can be well described by the traditional density functional calculations. However for the latter case the use of GGA+U method (for a review, see reference [9]) is especially suited, since it allows to introduce an on-site Coulomb repulsion term \(U\) and energy exchange term \(J\). Thus, for δ-Ce, the spin polarization and GGA+U correction are applied to compare with the normal GGA calculations without \(U\) correction. In practice, we chose the \(U\) and \(J\) values for δ-Ce, namely, 0.45 Ry and 0.05 Ry, respectively.

3. Results and discussion

To validate the computational scheme we chosen, the bulk modulus (\(B\)) and equilibrium volume (\(V\)) of δ-Ce are calculated and summarized in table 1. For comparison, limited experimental data [10] are also collected. It is clearly seen in table 1 that without \(U\) correction, the calculations failed to reproduce the bulk properties of δ-Ce completely. To compare with experimental data, the calculated \(V\) is underestimated badly, while the corresponding \(B\) is overestimated as well. As is expected, the results obtained by GGA+U scheme predict a bit smaller bulk modulus and the theoretical equilibrium volume is essentially in agreement with experiment. The errors between our results and experimental values are all less than 9%. Consequently, it is suggested that the 4\textit{f} electron in δ-Ce is correlated and localized, and the GGA+U method we employed to complete this studies is effective and reliable.

We now turn to the description of our results for the 4\textit{f} spectrum of δ-Ce (figure 1). The spin down 4\textit{f} spectrum is similar to the one of spin up. Our calculated 4\textit{f} spectrum comprises of two Hubbard side bands and several peaks around the Fermi level. The sharp peak at 5.0 eV is related to the upper Hubbard band, and the lower Hubbard band situates around -1.5 eV. As is seen in figure 1, the upper Hubbard band has larger weight than the lower Hubbard band. At Fermi level, the spectral weight of 4\textit{f} characters can be neglect entirely, i.e., the Kondo resonance peak is absent in δ-Ce. The resonance peak at Fermi level is the signature of Kondo screening of 4\textit{f} electron. Thus, in δ phase, the Kondo screening of 4\textit{f} electron is not significant. Because the spectroscopy measurements concerned with δ-Ce have not been reported by now, we compare its 4\textit{f} spectrum with the corresponding photoemission spectroscopy (PES) and Bremsstrahlung isochromatic spectroscopy (BIS) data of α and γ-Ce [11]. Clearly, the valence-band spectra of
both $\alpha$ and $\gamma$ phases consist of two Hubbard split bands and an pronounced Kondo resonance peak. The discrepancy of photoemission spectra between $\alpha$ and $\gamma$-Ce mainly lies in the spectral weight of the resonance peak. The Kondo peak in $\gamma$ phase has small weight and dramatically turns larger in $\alpha$ phase. The photoemission and Bremsstrahlung studies shown a remarkable transfer of spectral weight to the Fermi energy and the development of a large peak with its center of gravity slightly above the Fermi energy when going from $\gamma$ to $\alpha$-Ce phase. The greatly reduced but still extant spectral weight at Fermi level in $\gamma$-Ce, which is a more Kondo like feature, is in contrast to the completely absence of resonance peak in $\delta$ phase. From the evolution of $4f$ spectra of $\alpha$, $\gamma$, and $\delta$-Ce, it is argued that at lower volume ($\alpha$ phase) the $f$ electron is somewhat correlated, where the large resonance peak above the Fermi energy resembles the one-peak structure obtained by the traditional density functional calculations. At larger volume ($\gamma$ phase), the system is highly correlated, but the $f$ electron at the Fermi energy is neither fully delocalized nor fully localized. Finally at the largest volume ($\delta$ phase), the $f$ electron is localized and the local magnetic moment is fully developed. It is concluded that the smeared resonance peak in $\delta$-Ce may be related to the energetic changes in the correlation energy.

As a byproduct of this work, we calculated the complex dielectric function $\epsilon(\omega)$ of $\delta$-Ce. Using Kramers-Kronig relations and $\epsilon(\omega)$, any other optical property such as optical conductivity $\sigma(\omega)$, reflectivity $R(\omega)$, and refractivity can be accessed easily. In figure 2, the real dielectric function $\epsilon_1$ with energy is plotted. For optical properties of $\delta$-Ce, the reliable theoretical and experimental results are both desirable until now, so our results are predictive. The complex dielectric functions and additional several optical properties of $\alpha$ and $\gamma$-Ce have been determined lately by ellipsometry and grazing incidence reflectometry [12]. It should be useful and constructive to compare our results with their measured data. It is apparent that our results are in qualitative agreement with the trends observed in experimental curves, especially at high frequency region (>0.75 eV). Less satisfactory, at low energies our results predict positive values in contrast with experimental data. This distinctness between theory and experiment remains unclear. Nevertheless, let us concentrate on the energy dependence of real dielectric functions for $\alpha$, $\gamma$ and $\delta$-Ce. The peaks below 0.5 eV are response of Drude contribution. In $\alpha$ phase the Drude contribution is large and increases in intensity, leading to a more metallic-like behavior. Whereas in $\gamma$ and $\delta$ phases, the Drude peaks are much lower, and there are broad and almost featureless backgrounds. Due to localization, the $4f$ electrons of $\gamma$ and $\delta$-Ce have a negligible contribution.
Figure 2. Calculated real parts of complex dielectric functions of $\delta$-Ce.

to the low frequency spectral weight. As a result, it is reasonable that the Drude peaks in $\gamma$ and $\delta$ phases are lower than that in $\alpha$ phase, of which the itinerant 4$f$ electron contribute to the Drude peak. The difference of optical properties among different phases indicate again that $\gamma$ and $\delta$-Ce are highly correlated, yet $\alpha$-Ce is weakly correlated.

4. Conclusion

In this paper, we present first principles calculations for the bulk, electronic, and optical properties of $\delta$-Ce. The calculated bulk modulus and equilibrium volume are in good agreement with experiments. The 4$f$ partial density of states for $\delta$-Ce displays two-peaks structure near the Fermi level instead of three peaks. The Kondo resonance peak is not pronounced. The complex dielectric function of $\delta$-Ce is calculated as well. From the evolution of the 4$f$ spectra and optical properties for both $\alpha$, $\gamma$, and $\delta$ phases, it is argued that $\delta$-Ce is strongly correlated.

Acknowledgments

The authors wish to thank Dr. BingYun Ao for helpful discussions.

References

[1] Koskenmaki D C and Jr. Gschneidner K A 1978 Handbook on the Physics and Chemistry of Rare Earths (Amsterdam:North-Holland) chapter 4
[2] Johansson B 1974 Philos. Mag. 30 469
[3] Allen J W and Martin R M 1982 Phys. Rev. Lett. 49 1106
[4] Martin R M and Allen J W 1985 J. Magn. Magn. Mater. 47-48 257
[5] Allen J W and Liu L Z 1992 Phys. Rev. B 46 5047
[6] Blaha P, Schwarz K, Madsen K H, Kvasnicka D and Luitz J 2001 WIEN2K, An Augmented Plane Wave Plus Local Orbitals Program for Calculation Crystal Properties (Vienna University of Technology, Vienna, Austria) ISBN 3-9501031-1-2
[7] Schwarz K and Blaha P 2003 Compu. Mat. Sci. 28 259
[8] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[9] Anisimov V I and Lichtenstein A I 2000 Strong Coulomb Correlations in Electronic Structure Calculations (Amsterdam:Gordon and Breach Science Publishers) chapter 2
[10] Nicolaus K, Neuhaus J, Petry W, and Bossy J 2001 Eur. Phys. J. B 21 357
[11] Liu L Z, Allen J W, Gunnarsson O, Christensen N E, and Anderson O K 1992 Phys. Rev. B 45 8934
[12] van der Eb J W, Kuz’menko A B and van der Marel D 2001 Phys. Rev. Lett 86 3407