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Optical absorption and interband transitions in $CePd_7$

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A theoretical study of the optical absorption of $CePd_7$ is reported. The imaginary part of the dielectric function, as well as the optical conductivity, are calculated within the framework of the linear muffin tin orbital (LMTO) method. The origin of the different absorption peaks is attributed to particular interband transitions. In contrast to other Ce-Pd ordered alloys, it is found that $CePd_7$ behaves like an optical semiconductor (with an optical gap of 10 mRy) for the interband transitions. The results are analyzed in comparison with those of $CePd_3$ and $CePd_5$.

I. INTRODUCTION

The Ce-Pd intermetallic compounds have been extensively studied during the last few years. Three ordered alloys have been experimentally characterized: $CePd_3$, $CePd_5$, and $CePd_7$. From a fundamental point of view, the understanding of their electronic structures and optical properties has been the main goal. The four ingredients that give rise to the particular electronic distribution of each of the Ce-Pd alloys are the following: the relative position of the localized $4f$ states with respect to the $4d$ band, the hybridization between the Ce and Pd electronic states, the geometrical structure, and the relative concentration of Ce and Pd in the alloy. These factors, which are all related, are at the microscopic origin of macroscopic properties as, for instance, the resistivity. The electronic structures of $CePd_3$ and $CePd_7$ have been recently characterized (Refs. 1 and 2 and Ref. 3, respectively) and calculated with the linear muffin tin orbital (LMTO) method.[4,3] The agreement between theory and experiments is rather satisfactory. The site and orbital character of the high density regions of the electronic density of states (DOS) is clearly identified. In the same way, a theoretical study of $CePd_5$ by also using the LMTO method has been presented.[5] Up to now, the theoretical predictions concerning this alloy are waiting for an experimental confirmation. Some general trends are concluded from the systematical study of the electronic structure of the three phases. The charge transfer occurs from the Ce atom towards the Pd atoms, and at each Pd site its magnitude is directly related to the number of nearest Ce neighbors, irrespective of the geometrical structure. Besides, the localized $4f$ states which lie in the unoccupied region approach the Fermi energy as the Ce concentration increases and as a consequence, the DOS at the Fermi energy increases from $CePd_7$ to $CePd_5$ and $CePd_3$. This is confirmed experimentally for $CePd_3$ (Refs. 1 and 2) and $CePd_7$ (Ref. 3) through specific heat measurements.

The geometrical structure plays an important role in the optical response of the system. The optical absorption has been studied both experimentally[6,7] and theoretically,[4,8] only for $CePd_3$. The optical response for $CePd_5$ (Ref. 5) has been theoretically studied, but this study is lacking for $CePd_7$. It is the aim of the present work to complete the study of the optical properties in the Ce-Pd compounds. The optical absorption and optical conductivity is calculated for $CePd_7$. The origin of the different absorption peaks is attributed to particular interband transitions. The results are compared with the other alloys, and the new structures found only in $CePd_7$ are emphasized. Since the agreement between theory and experiments in the case of $CePd_3$ is quite good, we expect future experiments to confirm the prediction of this theoretical study. This paper is organized as follows. After a brief account of the theory for the optical response in the framework of the LMTO method, the results for the dielectric function and optical conductivity are analyzed. The main conclusions of the study are summarized in the last section.

II. OPTICAL ABSORPTION AND OPTICAL CONDUCTIVITY

The optical absorption of the system is directly proportional to the imaginary part of the dielectric function $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, ω being the photon frequency. Excluding the contribution of the intraband transition (the Drude term), which is only important at very low photon frequency ($\propto 1/\omega^3$), the optical absorption $\epsilon_2(\omega)$ incorporates the allowed interband transitions. In the limit of infinite lifetime of the excitation and at T=0 K, $\epsilon_2(\omega)$ is given by a surface integration in the Brillouin zone:

$$\epsilon_2(\omega)=\frac{e^2}{2\pi m^2\omega^2}\sum_{n,n'}\int_{\omega_{nn'}(\vec{k})=\hbar\omega}\frac{|\hat{e}\vec{P}_{nn'}(\vec{k})|^2}{|\vec{\nabla}\omega_{nn'}(\vec{k})|}d\vec{S}_k. \quad (1)$$

Here n and n' indicate the occupied and empty bands, respectively. The unit polarization vector of light is denoted by $\hat{e}$, and $\vec{P}_{nn'}(\vec{k})$ is the dipole matrix element between the occupied $|n\vec{k}\rangle$ and the empty $|n'\vec{k}\rangle$ states. These states have the eigenvalues $E_n(\vec{k})$ and $E_{n'}(\vec{k})$, respectively. Their difference $E_{n'}(\vec{k})-E_n(\vec{k})=\omega_{nn'}(\vec{k})=\hbar\omega$. The Brillouin zone integration is performed by using the usual tetrahedron technique. The above expression (1) involves a transition probability by means of the dipole matrix elements which obey the selection rules concerning the interband transition. The electronic structure is calculated by using the LMTO method in the atomic sphere approximation (ASA) including the combined correction.[9,10] The ASA is a good approxima-

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tion in these compact compounds where no empty spheres need be taken into account. The starting atomic potential is constructed with $4f^2 5d^0 6s^2$ for Ce and $4d^{10} 5s^0$ for Pd and s,p,d,f electrons are considered in the valence bands. The exchange and correlation potential has been treated in the local density approximation (LDA), within the von Barth–Hedin approximation.[11] Generally, the many-body effects play an important role in the localized states like $4f$ but the LDA approximation gives rather good results for these states in the Ce-Pd alloys.[12] The electronic structure of $CePd_7$ has been discussed in a previous work[3] and the agreement with the photoemission experiments is excellent. More details about the electronic structure calculation can be found in this reference.

In the general expression (1), the terms $|P_{nn'}(\vec{k})|^2$ contain the different orbital contributions allowed by the selection rules. In order to analyze the influence of the f states, one can decompose $\epsilon_2(\omega)$ as follows:

$$\epsilon_2(\omega)\equiv\epsilon_2^{spdf}(\omega)=\epsilon_2^{spd}(\omega)+\epsilon_2^{df}(\omega)+\epsilon_2^{spd-df}(\omega). \qquad (2)$$

$\epsilon_2^{spd}(\omega)$ is the total contribution of all the *spd* states. The $\epsilon_2^{df}(\omega)$ is due to the contribution of the *df* states, and the last contribution is the cross term of the *spd* and *df* which comes from the fact that we have to calculate the modulus squared of $P_{nn'}(\vec{k})$. The cross terms involving *spd* states appear also in $\epsilon_2^{spd}(\omega)$ and those involving *df* states appear in $\epsilon_2^{df}(\omega)$. Although experimentally these details can not be verified, it is interesting to penetrate the microscopic origin of the absorption peaks from the theoretical side. More relative to the experiments is the real part of the optical conductivity, which is directly calculated as $\sigma_1(\omega)=\omega\epsilon_2(\omega)/4\pi$.

III. RESULTS

The crystal structure of $CePd_7$ is characterized by a fcc unit cell with one Ce atom and seven Pd atoms.[13] There are two inequivalent types of Pd atoms. There is one Pd atom which has no Ce as its nearest neighbor, whereas each of the remaining six has two Ce atoms as nearest neighbors. This alloy has the lowest Ce concentration among the ordered Ce-Pd alloys characterized so far ($CePd_3$, $CePd_5$, $CePd_7$).

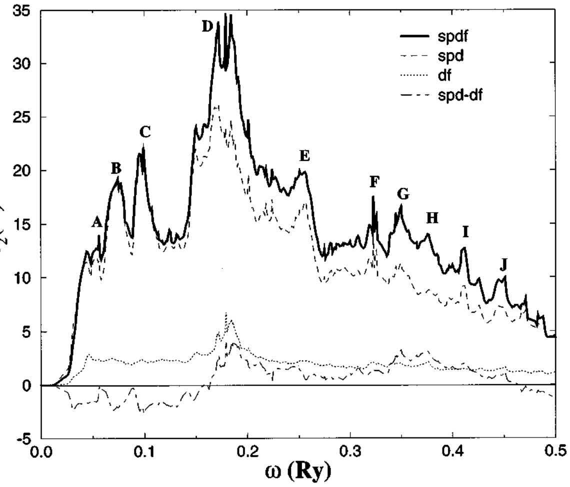

FIG. 1. The imaginary part of the dielectric function, $\epsilon_2(\omega)$, versus ω: total contribution of *spdf* (thick solid line), contribution of *spd* (dashed line), contribution of *df* (dotted line), and the cross contribution *spd−df* (dot-dashed line).

The results for the imaginary part of the dielectric function are shown in Fig. 1. A decomposition is made by separating the contribution to the interband transitions due to the *spd* transitions, the *df*, and the cross term as discussed in the preceding section. In this way, conclusions can be inferred about the orbital-orbital origin of the absorption peaks at the different energy regions. A very rich peak structure is obtained for the dielectric function as well as for the optical conductivity (Fig. 2). For our discussion, we have only selected the peaks lying at the photon energy lower than 0.5 Ry. However, since we have not taken into account the finite lifetime of the excitations, probably not all these peaks will be detected experimentally. In particular, peaks F, G, H, I, and J could be observed as a broad absorption peak with its maximum at the center of gravity of these five calculated peaks. The general shape of the dielectric function of $CePd_7$ is very different from that of $CePd_3$ (Refs. 4 and 8) and $CePd_5$,[5] particularly at the low-energy region ($\omega\leqslant 0.18$ Ry). In this low-energy region the optical absorptions of $CePd_3$ and $CePd_5$ are very intense and exhibit maxima. In contrast, in the case of $CePd_7$ the maximum of the optical absorption lies at around 0.18 Ry (peak D) and both the low- and high-energy region of the spectrum exhibits roughly the same height. The reason for this behavior can be understood by analyzing the orbital decomposition in Fig. 1. One notices that the origin of all the absorption peaks comes mainly from the *spd* interband transitions. The contribution from the *df* transitions is rather small and of the same order of magnitude along all the energy range. Moreover, in the low-energy region this *df* contribution cancels with the cross term *spd−df*. This behavior is rather different than that found in both $CePd_3$ (Refs. 4 and 8) and $CePd_5$,[5] where the $d\rightarrow f$ interband transition taking place in the Ce atoms contributed to a great extent to the optical absorption in the low-energy region. With respect to the high-energy region ($\omega>0.18$ Ry), the cross term contribution *spd−df* has positive sign and thus, the *spd* contribution to $\epsilon_2(\omega)$ lies lower than the sum of all contributions, as was the case also for $CePd_3$ and $CePd_5$. We can fully understand why the *df* contribution for energies lower than 0.18 Ry is negligible as compared to the case of $CePd_3$ and $CePd_5$ by analyzing the local density of states at the Ce atom and the relative Ce concentration of the three compounds. Indeed, the $d\rightarrow f$ and $f\rightarrow d$ interband transitions come from the Ce atoms, whose relative concentration with respect to Pd is smaller in $CePd_7$ than in $CePd_5$ or $CePd_3$. Thus, there will be a smaller relative contribution from the Ce atoms in $CePd_7$. Besides, the local density of states at the Ce atoms displays a rather small d character in the occupied states close to the Fermi energy, in contrast to the appreciable d character found for $CePd_5$ and $CePd_3$. Thus, the $d\rightarrow f$ and $f\rightarrow d$ interband transitions in the Ce atoms are rather improbable at photon energies $\omega<0.18$ Ry. From the above discussion, we can then attribute the origin of the absorption peaks A, B, C, D, and E mainly to the $d\rightarrow p$ interband transition in the Pd atoms and to a much lesser extent to $d\rightarrow f$ and $f\rightarrow d$ interband transitions in the Ce atom which can be neglected in a first aproximation. The $s\rightarrow p$ and

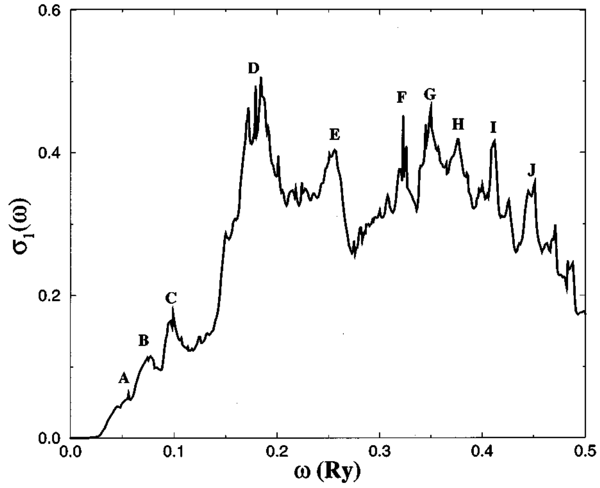

FIG. 2. The real part of the optical conductivity, $\sigma_1(\omega)$, versus ω. σ_1 is expressed in Ry (1 Ry=3.2885×10^{15} $\sec^{-1}$).

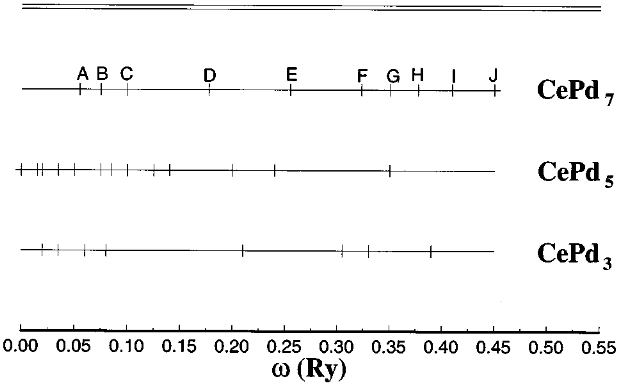

FIG. 3. The optical peak positions (in Ry) for $CePd_7$. The optical peaks for $CePd_3$ and $CePd_5$, taken from Refs. 8 and 5, respectively, are also reported in the same scale for the sake of comparison.

$p\rightarrow s$ transitions in the Pd atoms contribute also in the high-energy region (peaks F, G, H, I, and J). These $s\rightarrow p$ and $p\rightarrow s$ transitions start to be important when the photon energy is able to connect the bounded and the unbounded sp and ps states lying on the borders of the localized 4*d* band which has a bandwidth of about 0.3 Ry (where the sequence of peaks F, G, H, I, J starts). In Fig. 3, we report in the same energy scale the absorption peaks obtained for $CePd_7$ together with those previously found for $CePd_3$ and $CePd_5$. It is interesting to note that in the energy range above 0.3 Ry $CePd_7$ has more absorption peaks (Fig. 3) than $CePd_3$ and $CePd_5$. Since in the case of $CePd_3$ the agreement with the experimental results was rather satisfactory, we expect that the main absorption peaks for $CePd_7$ as well as for $CePd_5$ will also find experimental confirmation in the near future.

Another interesting feature of the dielectric function of $CePd_7$ that does not occur in other Ce-Pd compounds is the absence of optical absorption for photon energies lower than 10 mRy (see Fig. 1). This means that for the interband transitions to start, the energy of the radiation has to overcome this optical gap of 10 mRy. In this sense, $CePd_7$ behaves like an optical semiconductor in which there is no interband transition in this energy range. One can find the origin of this behavior in the electronic structure of $CePd_7$. Whenever the Fermi level crosses only the nondegenerate bands, the band-to-band transitions start only after an absorption edge. The same phenomenon is observed in many other similar cases like aluminium,[14,15] vanadium,[16] and sodium.[17] In this last case the band-to-band transition does not start before 2 eV. When there are degenerate bands at the Fermi level (as in the case of $CePd_3$ and $CePd_5$), this interband optically transparent behavior does not exist.[18–20] We wonder if this small optical gap could be observed experimentally after subtracting the contribution to the optical absorption spectrum due to the intraband transitions.

IV. SUMMARY

The optical absorption spectrum has been calculated for $CePd_7$ within the framework of the *ab initio* LMTO method. The origin of the absorption peaks of the dielectric function can be attributed mainly to the $d\rightarrow p$ interband transitions in Pd atoms. The $s\rightarrow p$ and $p\rightarrow s$ transitions in Pd contribute to a lesser extent for photon energies larger than 0.3 Ry. The contribution of $d\rightarrow f$ and $f\rightarrow d$ interband transitions in Ce is negligible. This behavior contrasts to that previously found in $CePd_3$ and $CePd_5$, where the Ce $d\rightarrow f$ and $f\rightarrow d$ interband transitions are appreciable, in particular at the low photon energy region of the spectrum. Also, in contrast to $CePd_3$ and $CePd_5$, the $CePd_7$ alloy behaves like an optical semiconductor with respect to interband transitions, with an optical gap of 10 mRy. It would be interesting in this respect to evaluate the effect of the electron-photon interaction on the optical gap, since in our calculation only k-conserving interband transitions are considered. We expect future experiments on $CePd_7$ to confirm the general features of the optical response presented in this work.

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