Evolution of carrier density in the series $YCu_{5-x}In_x$

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(Received 29 September 1995)

We present a study of the optical response of the series $YCu_{5-x}In_x$, with x varying from 0.97 to 1.1, in the spectral range 0.001–6 eV. The measured data show a large effect of the stoichiometry on the plasma frequency of these semimetallic compounds. The optical structures observed at energies above the plasma edge are investigated too. The results are discussed in terms of pressure effects, disorder, and electronic density of states.

I. INTRODUCTION

The intermetallic compounds RCu_4T, where R is a rare earth and T is a transition metal, have roused interest mainly for their magnetic and transport properties. Some of them crystallize into the cubic $C15b$ structure, with the R and T ions arranged in the face-centered positions of the zinc blende.[1]

Their interesting properties are related to the possible hybridization of the Rf electrons (in particular for R = Gd,Yb) with the conduction states, which yields to a large variety of phenomena such as magnetic order, Kondo interactions, and heavy-fermion behavior. In particular, $YbCu_4In$ shows a characteristic temperature-induced first-order phase transition from a local moment state at high temperature to an almost nonmagnetic state at low temperatures.[2–6] On the other hand, $YbCu_4Ag$ presents a typical Kondo-lattice behavior with a paramagnetic ground state,[7–9] while $YbCu_4Au$ and $YbCu_4Pd$ exhibit long-range magnetic order below 1 K.[8,10]

In the study of this class of compounds it is usually necessary to refer to the appropriate ''nonmagnetic'' compound (with R = Lu), which is expected to exhibit normal metallic behavior. Nevertheless, YCu_4In, which is nonmagnetic, shows an anomalous temperature-dependent resistivity $\rho(T)$. Beside a sudden decrease in $\rho(T)$ below $T \approx 7$ K due to the onset of superconductivity of a yet unknown phase, $\rho(T)$ exhibits a broad maximum around 270 K presumably originated by a semimetallic state.[11–13] Such a semimetal behavior, which has already been predicted for $YbCu_4In$, strongly depends on the position of the Fermi level in the system.[14] In turn, the Fermi energy is very sensitive to the degree of hybridization and to the number of carriers.

Optical spectroscopy is a suitable technique to study the changes in the density and the mobility of the carriers because it allows the determination of the plasma frequency as well as the energy and the intensity of the electronic excitations.

We measured the optical reflectivity of samples of the series $YCu_{5-x}In_x$ for x varying between 0.97 and 1.1, in order to investigate the electronic structure and to put into evidence the effects due to a change of stoichiometry on the carrier density and on the optical structures.

II. EXPERIMENT AND RESULTS

The samples were prepared from stoichiometric amounts of elements using high-frequency melting under a protective argon atmosphere. Subsequently, a heat treatment at $T = 750$ °C during 1 week, in argon atmosphere, was applied. The phase purity of the samples was checked using x-ray diffraction measurements. The lattice constant was found to be almost concentration independent (YCu_4In: $a = 7.193$ Å).

A shining optically cleaned surface of about 0.5 cm^2 was obtained on each sample by mechanical polishing with diamond powders.

Optical reflectivity of the samples was measured in the range 1 meV–0.6 eV (from far to near infrared) using a Fourier-transform spectrometer mod. Bruker IFS 113 V, and in the range 0.4–6 eV (from near infrared up to the ultraviolet) using a grating photospectrometer Varian mod. Cary 5.

Measurements were performed at room temperature and the results are shown in Fig. 1.

As we can notice, at the lowest energies all the compounds exhibit metallic behavior (high reflectivity values), but no well-defined trend can be noticed as the indium concentration changes.

The most relevant behavior is observed between 0.08 and 0.4 eV, where a fall of the reflectivity followed by a minimum occurs at different energies for the five samples. These features correspond to the plasma frequency of the respective compounds. The interesting fact is that this reflectivity minimum moves toward lower energies as the indium concentration increases. Correspondingly, the minimum itself becomes more sharp and an optical structure clearly emerges at about 0.2–0.3 eV for $YCu_{3.95}In_{1.05}$ and $YCu_{3.90}In_{1.10}$.

One reason the $YCu_{3.90}In_{1.10}$ reflectivity assumes little higher values in this spectral region could be that the preparation condition of this sample was different compared to the others.

At higher energies we observe some optical structures located at about 0.8, 1.3, 2, and 3.6 eV, then a further reflec-

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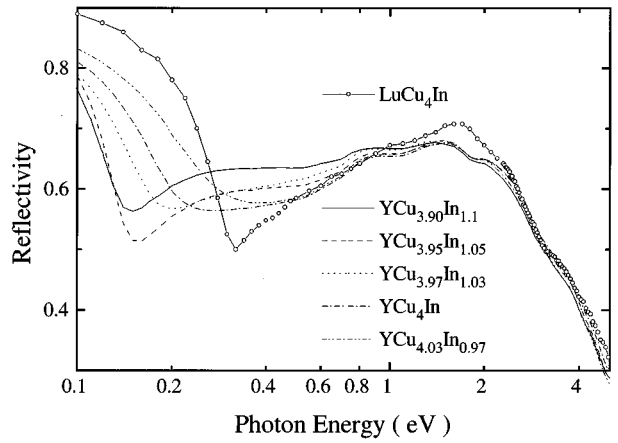

FIG. 1. Optical reflectivity of $YCu_{5-x}In_x$ for different values of substitution of copper with indium. For comparison the reflectivity of $LuCu_4In$ is shown too (circles).

tivity fall occurs, without showing any particular dependence on stoichiometry.

Kramers-Kronig analysis of the data has been carried on in order to obtain the real and imaginary parts of the complex dielectric function $\tilde{\epsilon}=\epsilon_1+i\epsilon_2$ from which the optical conductivity was obtained as $\sigma(\omega)=(\omega/4\pi)\epsilon_2$.

Below 1.5 meV an extrapolation based on the Hagen-Rubens formula was assumed in order to link up the results to the mesured values of the dc conductivity. Above 6 eV a conventional extrapolation with a term decreasing up to 18

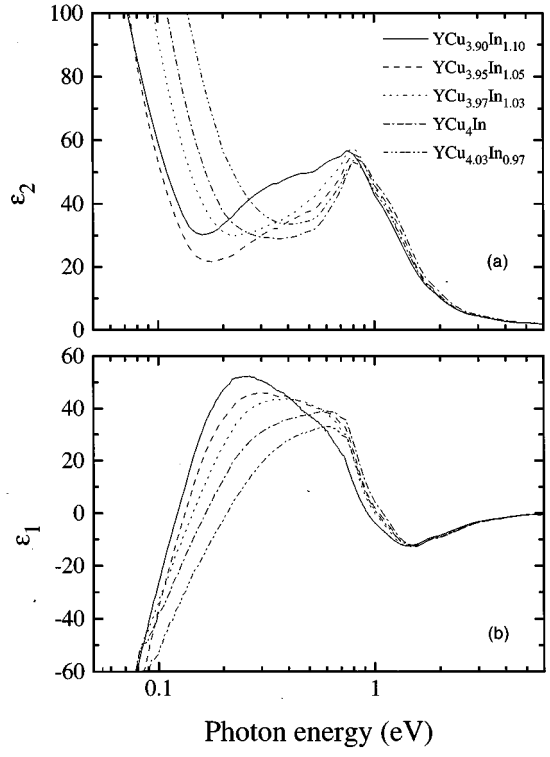

FIG. 2. Real (b) and imaginary (a) part of the dielectric function $\tilde{\epsilon}(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$ of $YCu_{5-x}In_x$ for different values of substitution of copper with indium.

TABLE I. Parameters obtained by the best fit of the optical results with a Drude term and four Lorentz oscillators. ω_i, γ_i, and f_i are, respectively, the resonance frequency, the bandwidth, and the oscillator strength of each oscillator.

$YCu_{5-x}In_x$	$x=1.10$	$x=1.05$	$x=1.03$	$x=1.00$	$x=0.97$
ω_p^2 (eV^2)	1.393	1.263	2.060	2.515	3.273
$\hbar\gamma_p$ (eV)	0.067	0.055	0.113	0.127	0.138
$\hbar\omega_1$ (eV)	0.295	0.299			
γ_1 (eV)	0.159	0.117			
f_1 (e/f.u.)	0.052	0.009			
$\hbar\omega_2$ (eV)	0.450	0.483	0.483	0.383	0.316
γ_2 (eV)	0.239	0.456	0.457	0.605	0.543
f_2 (e/f.u.)	0.117	0.028	0.212	0.132	0.123
$\hbar\omega_3$ (eV)	0.789	0.858	0.843	0.863	0.896
γ_3 (eV)	0.653	0.554	0.582	0.660	0.692
f_3 (e/f.u.)	1.288	1.073	1.203	1.198	1.311
$\hbar\omega_4$ (eV)	1.260	1.338	1.319	1.307	1.256
γ_4 (eV)	1.270	1.183	1.194	1.112	1.295
f_4 (e/f.u.)	2.146	2.416	2.274	2.328	2.220
ϵ_∞	2.92	3.30	3.82	4.04	4.46

eV as ω^2, then as ω^4 was used. Such spectral ''tails'' seem to be reasonable in our case; anyway they do not have any substantial effect on the energy region of interest in the infrared.

A plot of the dielectric functions ϵ_1 and ϵ_2 (Fig. 2) shows the plasma edge (cross of a zero value with positive slope) in the ϵ_1 spectrum, as well as the first minimum in ϵ_2 at low energy, separating the intraband from the interband contribution.

In order to obtain reliable values of the plasma frequencies of the compounds a simultaneous fit of ϵ_1 and ϵ_2 with the Drude model (accounting for the free carrier response) and four Lorentzian oscillators (accounting for interband transitions) has been performed in the energy range 0.05–2 eV, giving the results shown in Table I. The formulas used were

$$\epsilon_1(\omega)=\epsilon_\infty-\frac{\omega_p^2}{\omega^2+\gamma_p^2}+\frac{4\pi e^2N}{m_e}\sum_{j=1}^{4}\frac{f_j(\omega_j^2-\omega^2)}{(\omega_j^2-\omega^2)^2+(\gamma_j\omega)^2},$$

$$\epsilon_2(\omega)=\frac{\omega_p^2\gamma_p}{\omega(\omega^2+\gamma_p^2)}+\frac{4\pi e^2N}{m_e}\sum_{j=1}^{4}\frac{f_j\gamma_j\omega}{(\omega_j^2-\omega^2)^2+(\gamma_j\omega)^2},$$

where N is the density of Y atoms. The experimental dielectric functions are well reproduced by the fit. The discrepancies are on the order of 5% and became smaller than 1% for the copper-rich compounds. The differences between the calculated and the experimental reflectivities (less than 1%) are well within the experimental uncertainties. With respect to the error bars in the parameter determination we observed, in general, that a deviation of less than 10% of a parameter from the values presented in Table I would increase the χ^2 of the fit by one order of magnitude.

III. DISCUSSION

The data reported in the table give a quantitative description of the behavior reported above. The results suggest that some distinction should be made between the three samples corresponding to a slight or zero deviation from the exact stoichiometry ($x=0.97,1,1.03$) and the remaining two, which deviate to a larger extent from stoichiometry ($x=1.05,1.1$). In the first group some definite trends can be noticed in the behavior of the plasma frequency and of the nearest structure (at 0.31–0.48 eV). No well-defined changes can be identified for the structures at higher energy, apart from a small variation for the parameters of the structure at 0.85 eV.

In the two other samples a further structure must be accounted for at 0.3 eV, whereas the dependence on the stoichiometry of some parameters (e.g., the plasma frequency) is reversed.

It is interesting to notice that the sample dependence of the plasma frequency is reversed with respect to the expectations deduced from the resistivity (ρ) measurements according to $\rho \propto \gamma_p/\omega_p^2$. This means that, despite the changes in the effective carrier density, the main contribution to the sample dependence of the transport measurements is given by a different scattering rate $\gamma_p=1/\tau$ (τ is the scattering time). In effect, the values of γ_p obtained by the fit are in the correct order, but, except for $YCu_{3.9}In_{1.1}$ and $YCu_{3.95}In_{1.05}$, this is not enough in order to reproduce the trend observed in resistivity measurements. Moreover, the resistivities calculated using the data of Table I give values larger than the experimental ones.

Large uncertainties in the optical conductivity values at the lowest frequencies are, of course, expected when Kramers-Kronig analysis is applied to a metallic reflectivity. Anyway, our plasma frequency values were obtained at relatively high energies, where the characteristic reflectivity minimum marks the spectral features.

The discrepancies are probably due to the occurrence of phonon excitations, which open a further scattering channel for energies higher than 4–5 meV. As a matter of fact, reflectivity measurements exhibit vibrational structures at this energy. Such a problem has been partially considered in connection with the optical response of $YbCu_4In$.[15] It should require a closer inspection of the electron-phonon interaction in a semimetal, which would go far beyond the scope of the present communication. Then, we defer the problem to a further work and focus our attention on the optical response above 0.05 eV, whose analysis is, however, not affected by the relationship with transport measurements.

There are essentially three possibilities in which the stoichiometry changes can affect the electronic structures and the optical response of the series:

(i) At a first crude approximation the substitution of a copper atom with an indium one introduces two more electrons in the electronic states at the Fermi energy (E_F). On the other hand, the inverse substitution of indium with copper should subtract two electrons (or inject two holes). So, in a rigid band scheme, the effect should be a shift of E_F towards higher or, respectively, lower energies.

A good starting point to evaluate the consequences of such a shift follows from the band-structure calculation obtained for the isostructural and isoelectronic compound $LuCu_4In$.[14] In fact both the Lu and the Y compound can be classified as compensated semimetals, in agreement with the calculation results. The carrier concentration in YCu_4In has been found to be even lower than that in $LuCu_4In$;[12] this is probably due to a lower superposition of conduction and valence bands.

On the other hand the optical spectra of the two compounds are very similar (Fig. 1) showing features and structures corresponding in both cases, apart from a blueshift for $LuCu_4In$ with respect to YCu_4In.

By assuming the density of states (DOS) calculated for $LuCu_4In$ as at least qualitatively valid also for YCu_4In, we can evaluate the effect of a shift of E_F on the plasma frequency considering the expression

$$\omega_p^2 = \tfrac{8}{3}\pi e^2 \hbar^2 D(E_F)\langle v_F^2\rangle,$$

where $D(E_F)$ is the DOS at the Fermi level and v_F is the Fermi velocity.

Since the DOS around E_F is rapidly decreasing for increasing energies,[14] and assuming that v_F remains essentially constant, we deduce a ω_p dependence, which is in agreement with our result. It should also be possible to include in this scheme the ''anomalous'' behavior of $YCu_{3.90}In_{1.10}$. In fact the DOS, passing through a minimum, tends to increase again for a sufficiently large shift towards higher energies.

The same band structure can be used to assign the optical structures of ϵ_2 to transitions at defined critical points in the Brillouin zone, e.g., the main peak at about 0.85 eV could be ascribed to transitions at the center Γ of the Brillouin zone.

It is interesting that the lowest interband transition, detected at about 0.31 eV in $YCu_{4.03}In_{0.97}$, is shifting towards higher energies as the amount of indium increases. A shift of E_F could justify such a behavior if the excited states belong to a band that is crossing E_F (as, e.g., at Z).

(ii) A second possibility is a kind of pressure effect related to the variation of the lattice parameter due to the substitution. This effect has been considered as the main origin of the differences between $LuCu_4In$ and YCu_4In compounds, whose lattice constants are respectively 7.201 and 7.193 Å.[11] Such an effect should affect the whole electronic structure by changing the superposition of the bands and by shifting the energy of the critical points. As a matter of fact, this is not the case for the structures observed at the higher energies in the spectra measured at the different stoichiometries. We then conclude that this is not very relevant in our case.

(iii) The substitution of an atom with another of a different species can also be regarded as a sort of doping that introduces an impurity in the system.

Such an impurity acts in two ways. On one hand it provides some disorder by breaking the local symmetry of the unit cell. The effect of a distribution of impurities on the electronic structure can be described as a sort of folding of the Brillouin zone. In this way also indirect transitions, in principle, forbidden for optical excitation, can be activated by such a mechanism.

On the other hand, if the indium ion tends to lose its external three electrons (two more than copper), it remains and behaves as a charged impurity. The possibility of having bonded impurity electronic states in the vicinity of E_F is then open.

Both disorder and impurity effects are probably responsible for the low-energy structure detected in the two compounds, which are farther from the exact stoichiometry. Moreover, the strength of such a structure increases as the indium content increases.

IV. CONCLUSIONS

The results of optical measurements confirm the semimetallic character of $YbCu_{5-x}In_x$ compounds ($0.97 \leqslant x \leqslant 1.1$) and point out the strong dependence of the carrier density on Cu and In concentration. The main contribution to such a dependence is related to a shift of the Fermi level and to the subsequent change in the density of states at E_F. In the samples whose In concentration is further off from unity, disorder and impurity effects have been observed too.

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