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Infrared study of the valence transition compound $YbInCu_4$ using cleaved surfaces

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Optical reflectivity $[R(\omega)]$ of $YbInCu_4$ single crystals has been measured across its first order valence transition at $T_v \simeq 42$ K, using both polished and cleaved surfaces. $R(\omega)$ measured on cleaved surfaces $[R_c(\omega)]$ was found much lower than that on polished surface $[R_p(\omega)]$ over the entire infrared region. Upon cooling through T_v, $R_c(\omega)$ showed rapid changes over a temperature range of less than 2 K and showed only minor changes with further cooling. In contrast, $R_p(\omega)$ showed much more gradual and continuous changes across T_v, similar to previously reported data on polished surfaces. The present result on cleaved surfaces demonstrates that the microscopic electronic structures of $YbInCu_4$ indeed undergo sudden changes upon the valence transition, which is consistent with its first order nature. The gradual temperature evolution of $R_p(\omega)$ is most likely due to the compositional and/or Yb-In site disorders caused by polishing.

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Physical properties of strongly correlated "heavy fermion" compounds, most typically Ce-or Yb-based compounds containing a partly filled $4f$ shell, have attracted much attention.[1] The hybridization between the conduction (c) electrons and the otherwise localized f electrons leads to many interesting phenomena. Among them is a duality and crossover between itinerant and localized characters of the f electrons.[2] An important characteristic energy for the c-f hybridization is the Kondo temperature (T_K). At temperatures (T) well above T_K, f electrons are basically localized, resulting in local moment (Curie-Weiss) paramagnetism. With decreasing T, the c-f hybridization becomes progressively stronger. At $T \ll T_K$, the local moment is well-screened, and a spatially extended, coherent band is formed. Due to the strong Coulomb correlation of f electrons, the resulting bands show enhanced effective masses and a Pauli paramagnetism with a large effective moment. Associated with this crossover from localized to itinerant characteristics, the average valence of Ce or Yb ions deviates from 3 (decreases for Yb and increases for Ce).

Usually, such a T-induced crossover between localized and itinerant regimes is continuous, and marked by, e.g., a broad maximum in the T-dependence of susceptibility and/or the f electron-derived resistivity.[2] However, $YbInCu_4$ undergoes a first-order phase transition at $T_v \sim 42$ K between the high T phase (HTP) in a localized regime with $T_K = 20$ K and the low T phase (LTP) in an itinerant regime with $T_K = 300$ K.[3,4] Upon cooling through T_v, $YbInCu_4$ shows discrete changes in the lattice constant and many other physical properties. The Yb valence deduced from measured bulk thermodynamic properties is almost 3 in HTP, and about 2.9 in LTP. It is an intriguing question as to why this particular compound shows such a first-order transition between the two regimes, while most others show only continuous and gradual crossovers. Several models have been proposed as the origin for the transition.[5]

To understand the microscopic nature of such an electronic transition, it is important to probe the electronic structures around the Fermi level (E_F). For this purpose, infrared (IR) reflectivity $[R(\omega)]$ of $YbInCu_4$ has been measured in detail, at temperatures both above and below T_v.[6–9] $R(\omega)$ showed large changes between LTP and HTP. In the optical conductivity $\sigma(\omega)$ obtained from $R(\omega)$, a marked mid-IR peak was observed in LTP, which was interpreted[7] as arising from optical excitations in the c-f hybridized state.[10] This optical result demonstrated that the microscopic electronic structures around the Fermi level indeed undergo large changes upon the valence transition. However, the observed $R(\omega)$ seemed to show gradual variations upon cooling through T_v.[9] Such a T dependence is in contrast to the first-order nature of the transition.

Interesting results have been also reported concerning the Yb valence in $YbInCu_4$ studied by photoemission spectroscopy (PES).[11–13] In early PES studies on scraped surfaces with a vacuum UV source,[11] where the escape depth of photoelectrons was small, only a gradual change of valence was observed across T_v, and the valence was much lower than that given by the bulk properties. However, as the escape depth increased with soft and hard x-ray sources and as the sample was prepared by cleaving (fracturing), a much sharper change of valence was observed, and the valence was much closer to the bulk values.[12,13] These PES results strongly suggest that the valence and its transition in $YbInCu_4$ are extremely sensitive to disorder, caused either by scraping or by the presence of the surface itself.

Motivated by the above developments, we have measured infrared $R(\omega)$ of $YbInCu_4$ *using both polished and cleaved surfaces* of single crystals taken from the same batch, and have tried to obtain intrinsic $\sigma(\omega)$ of $YbInCu_4$. Although the $R(\omega)$ spectra measured on cleaved surfaces $[R_c(\omega)]$ had qualitatively similar spectral shapes to those on polished surfaces $[R_p(\omega)]$, the magnitude and T dependences were remarkably different between $R_c(\omega)$ and $R_p(\omega)$. With decreasing T, $R_c(\omega)$ showed sudden spectral changes at T_v, while $R_p(\omega)$ showed only gradual changes. The variations of $R_c(\omega)$ are very consistent with the first-order nature of the transition

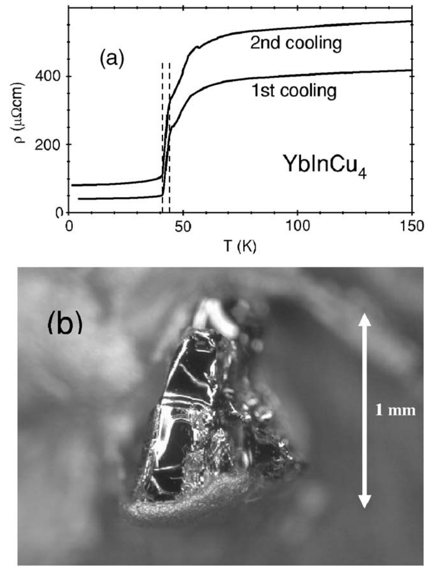

FIG. 1. (a) Resistivity (ρ) of YbInCu$_4$ single crystal as a function of temperature (T). Two vertical lines indicate 41 and 44 K. (b) Photograph of cleaved (fractured) surfaces of a YbInCu$_4$ single crystal. The dark areas indicate flat, specular surfaces.

and demonstrate that the microscopic electronic structures in YbInCu$_4$ indeed undergo a sudden change at T_v. We analyze the origin of gradual changes in $R_p(\omega)$ in terms of microscopic disorder caused by polishing.

The samples used in this work were single crystals grown by an In-Cu self-flux method, similarly to that previously described.[4] The resistivity of the single crystal decreased rapidly between 41 and 44 K, as shown in Fig. 1(a), consistent with the reported value of T_v=42 K. The higher resistivity of the second cooling cycle is also consistent with that reported previously.[4] This increase of resistivity after the first temperature cycle was attributed[4] to internal strain caused by the lattice contraction upon warming through T_v. To obtain cleaved surfaces, a block of single crystal was fractured into small pieces. They had flat, specular surfaces only with small dimensions (typically 50–500 μm). Those having such specular surfaces were mounted in a continuous-flow liquid He cryostat. The photograph of a measured sample is shown in Fig. 1(b). $R_c(\omega)$ spectra of thus mounted samples were measured using an IR microscope and an IR synchrotron radiation (SR) source at the beam line BL43IR of SPring-8.[14] Owing to the high brilliance of IR-SR, it was possible to focus the beam to a spot of ~15 μm diameter at the sample without using any aperture in the optical path. This enabled us to easily measure $R_c(\omega)$ of the small specular surfaces of YbInCu$_4$. To obtain $R_p(\omega)$, the crystals taken from the same batch as those used for $R_c(\omega)$ were mechanically polished. $R_p(\omega)$ were measured using an apparatus without a microscope, as previously described.[16] $R_p(\omega)$ were measured up to 30 eV using a SR source at the beam line BL7B of UVSOR, Institute for Molecular Science. $\sigma(\omega)$ spectra were obtained from the measured $R(\omega)$ spectra using the Kramers-Kronig relations.[17] Due to a technical restriction, $R_c(\omega)$ spectra were measured at 0.06–2 eV only, above which they were smoothly connected to $R_p(\omega)$. Below the measured range, $R_c(\omega)$ and $R_p(\omega)$ were extrapolated using the Hagen-Rubens relation.[17]

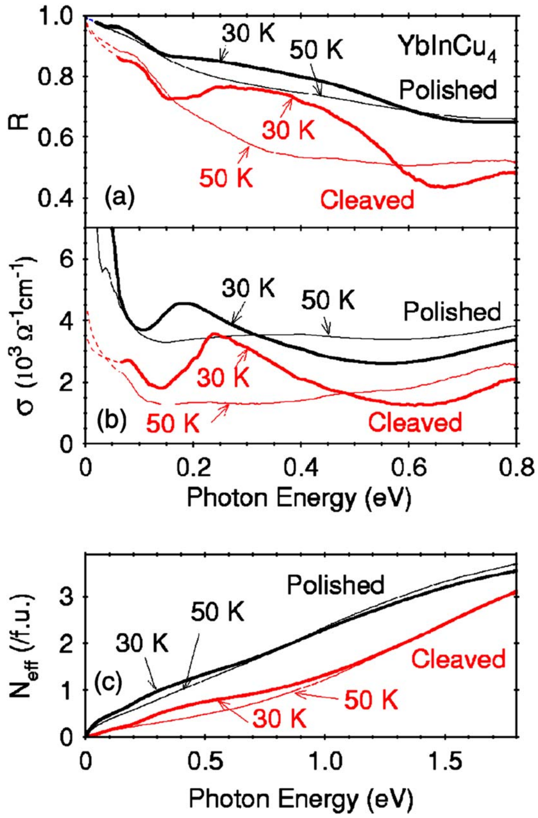

FIG. 2. (Color online) (a) Reflectivity spectra (R) of YbInCu$_4$ measured on cleaved and polished surfaces above and below T_v. (b) Optical conductivity spectra (σ) obtained from the reflectivity using the Kramers-Kronig relations. The spectra in the extrapolated region are indicated by broken curves. (c) Effective carrier density N_{eff} per formula unit (f.u.) calculated from $\sigma(\omega)$ using the optical sum rule.

Figure 2(a) shows $R_c(\omega)$ and $R_p(\omega)$ in HTP and LTP. The spectral shapes of $R_c(\omega)$ and $R_p(\omega)$ are qualitatively similar to each other. Namely, in the high-T phase the spectrum is a decreasing function of photon energy. In the low-T phase, on the other hand, the reflectivity at 0.2–0.55 eV increases significantly and shows a marked dip centered at ~0.15 eV. These spectral variations are qualitatively similar to previous results.[7–9] However, the over all magnitude of $R_c(\omega)$ is much lower than that of $R_p(\omega)$. We have carefully confirmed that the low value of $R_c(\omega)$ is not due to experimental errors, but an intrinsic property of the cleaved surfaces.[15] In addition, the difference in $R_c(\omega)$ between the two phases is much larger than that in $R_p(\omega)$. Figure 2(b) shows the optical conductivity spectra of the cleaved $[\sigma_c(\omega)]$ and polished $[\sigma_p(\omega)]$ samples, obtained from $R_c(\omega)$ and $R_p(\omega)$, respectively. They show a large difference in their magnitude, corresponding to that between $R_c(\omega)$ and $R_p(\omega)$, while their spectral shapes appear qualitatively similar to each other. It appears as though $\sigma_p(\omega)$ results from the superposition of a constant background upon $\sigma_c(\omega)$. Note, however, that the mid-IR peak energy of 0.25 eV in $\sigma_c(\omega)$ is about 70 meV higher than in $\sigma_p(\omega)$. In previous works on polished samples, the

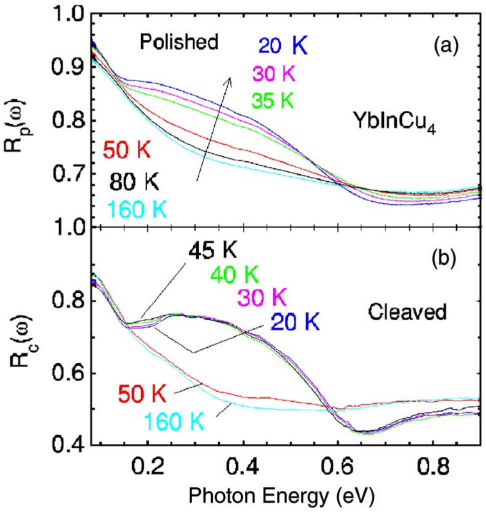

FIG. 3. (Color online) Reflectivity spectra of $\mathrm{YbInCu_4}$ single crystals measured on (a) polished and (b) cleaved surfaces. Note that the vertical scale is different between (a) and (b).

mid-IR peak in $\sigma(\omega)$ was centered at ~ 0.25 eV,[8,9] and at ~ 0.3 eV ($\sim 2500\ \mathrm{cm}^{-1}$).[7] Figure 2(c) shows the effective carrier density $N_{\mathrm{eff}}(\omega) = (2m_0/\pi e^2)\int_0^{\omega}\sigma(\omega')d\omega'$ given by the optical sum rule.[17] The sum rule is satisfied (the spectral weight transfer is completed) at 1.3 eV for the cleaved sample, since N_{eff} below T_v is almost equal to that above T_v for $\hbar\omega \geqslant 1.3$ eV. In contrast, it is not satisfied up to 1.8 eV for the polished sample.

Figure 3 compares the detailed T dependences of $R_c(\omega)$ and $R_p(\omega)$. $R_p(\omega)$ changes gradually with decreasing T, and keeps changing even below 40 K. These spectral evolutions agree well with those previously reported for polished surfaces.[9] The $R_c(\omega)$ spectra, on the other hand, show large changes over a very narrow T range. In addition, $R_c(w)$ is almost unchanged in LTP, with only minor variations in the shape of the dip. Clearly, the T-dependence of $R_c(\omega)$ is quite different from that of $R_p(\omega)$. In Fig. 4, to show their T variations more quantitatively, $R_c(\omega)$ and $R_p(\omega)$ integrated at 0.2–0.55 eV are plotted as a function of T. It is seen that the change in $R_c(\omega)$ occurs at ~ 46 K over a T range of less than 2 K, in contrast to the gradual change of $R_c(\omega)$.[18] While the T variation in $R_c(\omega)$ is as sharp as that in the resistivity, the transition T of 46 K implied by $R_c(\omega)$ is slightly higher than 41–44 K implied by the resistivity [Fig. 1(a)]. The variations of integrated $R_c(\omega)$ with T was accompanied by a hysteresis of about 1 K. Such a hysteresis is consistent with those observed in the thermodynamic properties. Another interesting feature in Fig. 4 is that no significant difference is observed in $R_c(\omega)$ between the first and second cooling cycles, in contrast to the different resistivities for the first and second coolings [see Fig. 1(a)].

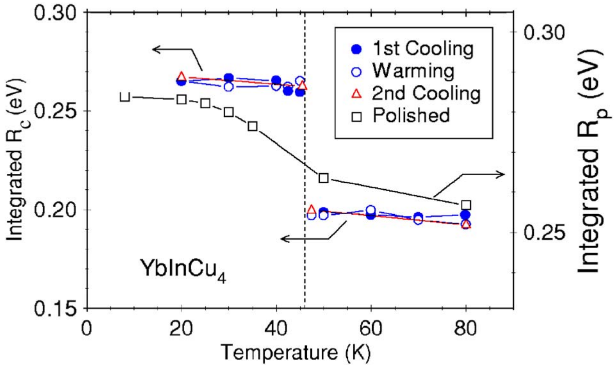

FIG. 4. (Color online) $R_c(\omega)$ and $R_p(\omega)$ integrated from 0.2 to 0.55 eV as a function of temperature. The vertical line is drawn at 46 K and is a guide to the eye.

Clearly, the T evolution of $R_c(\omega)$ is more consistent with the first-order nature of the valence transition, and with the T variations of other physical properties such as resistivity and susceptibility, which change suddenly upon the transition and remain almost constant below T_v. Hence the $R_c(\omega)$ data should reflect the intrinsic bulk electronic structures of $\mathrm{YbInCu_4}$ more closely and directly than the $R_p(\omega)$ data. However, as mentioned before, the spectral shape of $\sigma_c(\omega)$, in particular the mid-IR peak in LTP, is qualitatively similar to that in $\sigma_p(\omega)$. Hence the interpretation of $\sigma(\omega)$ in LTP in terms of a c-f hybridized state reported in the previous works[7–9] should remain valid. The origin for the spread of mid-IR peak energies (0.18–0.3 eV) for polished samples in this work and in the previous works[7,8] is unclear. It may have resulted from differences in the specific way the polishing was done in these works. On the other hand, the magnitude and T-dependence of $\sigma_c(\omega)$ are quite different from those of $\sigma_p(\omega)$. Therefore the previous data on the spectral weight and its T-induced transfer in $\sigma(\omega)$ measured for polished $\mathrm{YbInCu_4}$ should be interpreted carefully.[7,9]

The broadened T dependence in $R_p(\omega)$ should be due to disorder introduced by the mechanical polishing. Two kinds of disorder are likely to be responsible: a deviation from the ideal 114 composition and a site disorder. Since the early stage of research on $\mathrm{YbInCu_4}$, it has been recognized that the T_v value for $\mathrm{Yb_{1-x}In_{1+x}Cu_4}$ is a sensitive function of x.[3] Such a compositional disorder is quite likely to result from mechanical polishing, which may lead to a distribution of T_v within the penetration depth of the IR radiation. The penetration depth of $\mathrm{YbInCu_4}$ in the photon energy range of 0.1 to 0.2 eV has been estimated to be 500–1000 Å from the absorption coefficient obtained with the Kramers-Kronig analysis of $R_c(\omega)$ and $R_p(\omega)$. In addition, even in high-quality $\mathrm{YbInCu_4}$ samples with a negligible compositional deviation, a site disorder tends to occur between the In and Yb sites (Yb occupying In site, and vice versa).[19] It has been pointed out that such a site disorder may change the Yb valence and the T_v value.[19] It is likely that the surface layer of a mechanically polished sample has more site disorder, and hence a broader transition, than that of a cleaved surface. We believe that the broadened T variation of $R_p(\omega)$ results from the compositional and/or site disorder.

Note that the sudden change of $R_c(\omega)$ occurs at 46 K, in contrast to 41–44 K in the resistivity. This is a rather unexpected result, since it is natural to expect $R(\omega)$ and resistivity to change at the same transition temperature. The origin for this difference is unclear at the present time. One possibility is that T_v is sensitive even to the cleaving, so that the T_v becomes slightly higher at the near-surface region [without, however, a distribution of T_v since the T variation of $R_c(\omega)$ itself is very sharp]. Further study is needed to clarify this point.

In addition to the different T dependences, $R_c(\omega)$ has much lower magnitude than $R_p(\omega)$ at all measured T's, as mentioned above. Since the higher $R_p(\omega)$ has been caused by polishing, it is also likely due to disorder. The higher $R_p(\omega)$ probably results from higher reflectivity of the composition-disordered or site-disordered portion of $YbInCu_4$ in the surface layer. It is even likely that some fraction of the disordered portion at the surface does not undergo the valence transition, hence contributing a T-independent, constant background in $R(\omega)$ and $\sigma(\omega)$.

In conclusion, IR reflectivity spectra of $YbInCu_4$ have been measured on cleaved and polished surfaces of single crystals. The reflectivity spectrum measured on the cleaved surface showed sudden changes over a narrow T range upon the valence transition, in contrast to the gradual T evolution observed for polished surfaces. The result on the cleaved surface demonstrates that the microscopic electronic structures in $YbInCu_4$ indeed undergo a first-order transition. The broadened T evolution of reflectivity for the polished sample has been analyzed in terms of compositional and/or Yb-In site disorder caused by polishing.

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[1] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, England, 1993).

[2] See, for example, J. M. Lawrence, P. S. Riseborough, C. H. Booth, J. L. Sarrao, J. D. Thompson, and R. Osborn, Phys. Rev. B **63**, 054427 (2001).

[3] I. Felner and I. Nowik, Phys. Rev. B **33**, 617 (1986).

[4] J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 12207 (1996).

[5] A. L. Cornelius, J. M. Lawrence, J. L. Sarrao, Z. Fisk, M. F. Hundley, G. H. Kwei, J. D. Thompson, C. H. Booth, and F. Bridges, Phys. Rev. B **56**, 7993 (1997), and references cited therein.

[6] V. N. Antonov, M. Galli, F. Marabelli, A. N. Yaresko, A. Ya. Perlov, and E. Bauer, Phys. Rev. B **62**, 1742 (2000).

[7] S. R. Garner, J. N. Hancock, Y. W. Rodriguez, Z. Schlesinger, B. Bucher, Z. Fisk, and J. L. Sarrao, Phys. Rev. B **62**, R4778 (2000).

[8] J. N. Hancock, T. McKnew, Z. Schlesinger, J. L. Sarrao, and Z. Fisk, Phys. Rev. Lett. **92**, 186405 (2004).

[9] J. N. Hancock, T. McKnew, Z. Schlesinger, J. L. Sarrao, and Z. Fisk, Phys. Rev. B **73**, 125119 (2006).

[10] D. L. Cox, Phys. Rev. Lett. **58**, 2730 (1987), and references therein.

[11] F. Reinert, R. Claessen, G. Nicolay, D. Ehm, S. Hüfner, W. P. Ellis, G.-H. Gweon, J. W. Allen, B. Kindler, and W. Assmus, Phys. Rev. B **58**, 12808 (1998). See also the references cited in Refs. 12 and 13.

[12] H. Sato, K. Yoshikawa, K. Hiraoka, M. Arita, K. Fujimoto, K. Kojima, T. Muro, Y. Saitoh, A. Sekiyama, S. Suga, and M. Taniguchi, Phys. Rev. B **69**, 165101 (2004).

[13] H. Sato, K. Shimada, M. Arita, K. Hiraoka, K. Kojima, Y. Takeda, K. Yoshikawa, M. Sawada, M. Nakatake, H. Namatame, M. Taniguchi, Y. Takata, E. Ikenaga, S. Shin, K. Kobayashi, K. Tamasaku, Y. Nishino, D. Miwa, M. Yabashi, and T. Ishikawa, Phys. Rev. Lett. **93**, 246404 (2004).

[14] S. Kimura, T. Nanba, T. Sada, M. Okuno, M. Matsunami, K. Shinoda, H. Kimura, T. Moriwaki, M. Yamagata, Y. Kondo, Y. Yoshimatsu, T. Takahashi, K. Fukui, T. Kawamoto, and T. Ishikawa, Nucl. Instrum. Methods Phys. Res. A **467–468**, 893 (2001).

[15] To calibrate the absolute value of $R_c(\omega)$, we compared reflectivities of a specular portion before and after coating the sample with Au. By doing this, one can remove effects due to an irregular surface, as previously discussed by C. Homes, M. A. Reedyk, D. A. Crandels, and T. Timusk, Appl. Opt. **32**, 2976 (1993). In addition, we also measured the reflectivity of a large, polished sample using the same IR microscope. The spectrum agreed with $R_p(\omega)$ measured by the nonmicroscope apparatus. These results show that the low value of $R_c(\omega)$ is neither due to diffraction arising from the microscope nor due to irregular sample surfaces.

[16] H. Okamura, T. Michizawa, T. Nanba, and T. Ebihara, J. Phys. Soc. Jpn. **73**, 2045 (2004).

[17] M. Dressel and G. Gruner, *Electrodynamics of Solids* (Cambridge University Press, Cambridge, England, 2002).

[18] Although the $R_p(\omega)$ spectra were recorded only at selected T's, the total reflection intensity was continuously monitored throughout the cooling and warming processes. No steep change of the reflectivity was observed around T_v, unlike the case of $R_c(\omega)$.

[19] J. M. Lawrence, G. H. Kwei, J. L. Sarrao, Z. Fisk, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 6011 (1996).