Enhanced far-infrared absorption in $CePd_3$ and $YbCu_2Si_2$.
III. Comparison of a resonant-scattering model with experiment

F. E. Pinkerton, B. C. Webb, A. J. Sievers, and J. W. Wilkins

Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

L. J. Sham

Department of Physics, University of California—San Diego, La Jolla, California 92093

We present a model calculation for the low-energy ($\sim$10-meV) optical conductivity of valence-fluctuation compounds for the case of resonant scattering of conduction electrons from a scattering level lying within 10 meV of the Fermi energy. The model is characterized by an enhancement of the optical absorption in the far infrared over that of a normal metal, and it agrees reasonably well with the measured low-temperature optical conductivity of $CePd_3$ and $YbCu_2Si_2$ with suitable choices of the model parameters. In the case of $CePd_3$, in which optic phonons are observed, the effects of including the optic-phonon modes in the model calculations are also discussed.

I. INTRODUCTION

Experimental measurements of the far-infrared absorption in valence fluctuating (VF) materials have produced anomalous results.[1] In particular, the absorptivities of $CePd_3$ and $YbCu_2Si_2$ at helium temperature show a broad peak near 20 meV. In this paper we present a model calculation for the optical conductivity due to resonant scattering of conduction electrons from a level near the Fermi energy and then compare this model calculation directly with the experimental data given in Ref. 1 (hereafter referred to as paper I). With a suitable choice of model parameters fairly good agreement is found with the measured low-temperature optical conductivity of $CePd_3$ and $YbCu_2Si_2$.

It was suggested in paper I that the optical absorption of $CePd_3$ and $YbCu_2Si_2$ could be roughly fitted by a frequency-dependent conduction-electron scattering rate $1/\tau(\omega)$ with a resonant form. Such a form for the real quantity $\tau(\omega)$ represents an oversimplified expression for resonant-level scattering. In Sec. II we describe a more complete calculation of the complex optical conductivity $\sigma(\omega)$ corresponding to conduction electrons scattering resonantly from a level at or near the Fermi level E_F. The optical absorption predicted by this model successfully fits the observed low-temperature frequency-dependent absorptivity of $CePd_3$ and $YbCu_2Si_2$. Optic phonons are included in the resonant-level model fits in Sec. III by adding the phonon contribution calculated in paper II of this series.

II. RESONANT-LEVEL-MODEL CONDUCTIVITY FOR A VALENCE FLUCTUATOR

There is no theoretical model commonly agreed on for a valence fluctuator. Those models sufficiently rich to give a nontrivial optical conductivity $\sigma(\omega)$ have so far resisted a calculation of it. Accordingly, we consider the simplest nontrivial model: treating a resonant level (RL)

with position E_r (relative to the Fermi level) and width Γ. Then the self-energy of conduction-electron scattering off a density n_i of such "impurities" is

$$\Sigma(E) = \frac{S\Gamma/2}{E - E_r + i\Gamma}, \tag{1}$$

where $S \simeq 2n_i(\pi N(0)/\Omega)$, $N(0)$ being the density of conduction states per spin at the Fermi level and Ω is the volume. We observe, in passing, that identification of $-2\,\text{Im}\Sigma(E)$ with an inverse scattering rate $1/\tau(E)$ would give

$$\frac{1}{\tau(E)} = \frac{S\Gamma^2}{(E - E_r)^2 + \Gamma^2}. \tag{2}$$

This simple form has already been used in a preliminary[1-3] analysis of the $CePd_3$ data. That resulting fit is quite good except above the resonance at 20 meV where the theory curve falls too rapidly with increasing energy. Because Eq. (2) includes only the imaginary part of $\Sigma(E)$, however, the optical properties calculated from this simple form do not necessarily satisfy the Kramers-Kronig relations. Accordingly, we consider a more detailed examination of $\sigma(\omega)$ arising from the self-energy Eq. (1) for which $\sigma(\omega)$ automatically obeys the Kramers-Kronig relations.

In addition to scattering off the resonant level we suppose that there is an additional frequency-independent scattering rate $1/\tau_0$ describing the disorder scattering present in simple metals, and which is in fact responsible for much of the dc resistance. Then the conductivity due to this and the self-energy Eq. (1) can be written

$$\sigma(\omega) = \frac{ne^2}{m} \int dE \frac{[f(E-\omega) - f(E)]/\omega}{\omega + \dfrac{i}{\tau_0} - \Sigma(E) + \Sigma^*(E-\omega)}, \tag{3}$$

where $f(E)$ is the Fermi function $(e^{\beta E} + 1)^{-1}$, with $\beta \equiv 1/k_B T$. [Note that if Σ is set to zero, (3) reduces to

the Drude result $\sigma(\omega)=ne^2\tau_0/m\,(1-i\omega\tau_0)$.] The prefactor is derived from the plasma frequency $\omega_p^2=4\pi ne^2/m$. For $kT \ll E_r$ we can consider only the zero-temperature limit where the difference of the Fermi factors reduces the integral range to $0 < E < \omega$.

First consider a very simple approximation to Eq. (3)—namely, we replace the integrand by its value at the midpoint of the interval. Then

$$\sigma(\omega)=\frac{ine^2/m}{\omega+i\{(1/\tau_0)-[S\Gamma(\Gamma-i\omega/2)]/[(i\Gamma+\omega/2)^2-E_r^2]\}} \cdot$$
(4)

Note that the curly bracket is an effective relaxation time that looks rather similar to the sum of $1/\tau$ plus Eq. (2), i.e., to what was used in the earlier analysis.[2,3] Note, however, that for large ω it falls off as $1/\omega$ and not $1/\omega^2$ as does Eq. (2); accordingly, this form will be more successful at fitting the high-frequency absorptivity.

For our actual analysis we have performed the integral in Eq. (3) to obtain

$$\sigma(\omega)=\frac{ine^2/m}{\omega+i/\tau_0}\left[1+\frac{iV^2}{2\omega W}\ln\frac{[(\omega/2)-iW]^2-E_r^2}{[(\omega/2)+iW]^2-E_r^2}\right],\quad(5)$$

where

$$V^2=\tfrac{1}{2}S\Gamma\frac{\omega+2i\Gamma}{\omega+i/\tau_0}$$
(6)

and

$$W^2=V^2-(i\Gamma+\omega/2)^2 .$$
(7)

Equation (3) has no ambiguity in phase but to perform the integral square roots are taken which introduce branch questions. The branches of the ln in Eq. (5) are chosen so that $\sigma(\omega)$ is a continuous function of ω. This means that the final result of the ln term must be continuously extended from $-\pi/2$ to $\pi/2$.

Equations (5)–(7) give the optical conductivity of the resonant-level model. Note that the Eq. (5) for $\sigma(\omega)$ is even in E_r, thus the model cannot distinguish whether the resonance is above or below E_f.

The absorptivity of the resonant-level model is calculated according to

$$A(\omega)=4\,\mathrm{Re}\left[\frac{1}{\epsilon(\omega)}\right]^{1/2},\quad(8)$$

where $\epsilon(\omega)=1+4\pi i\sigma(\omega)/\omega$ is the dielectric function (see paper I). The best fit of this model to the measured absorptivity of etched CePd₃ (see paper I, Fig. 6) is the dashed curve in Fig. 1. The parameters of the fit are given in Table I. The fit is quite good throughout the frequency region. The conductivity at $\omega=0$ corresponds to a
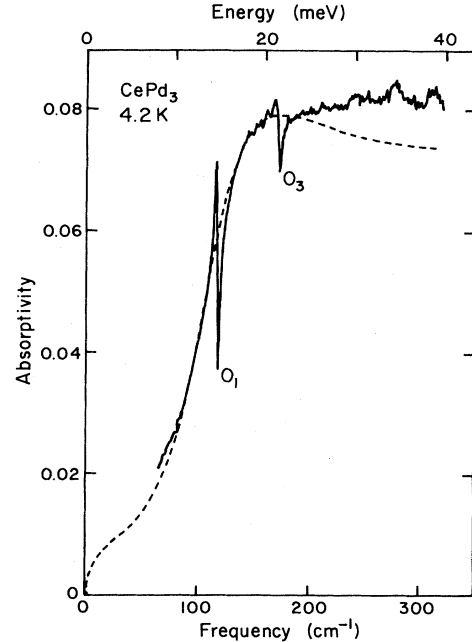

FIG. 1. Model fits to the absorptivity of CePd₃ at 4 K. The solid curve is the experimental absorptivity. O_1 and O_3 denote the infrared-active optic-phonon modes. The dashed curve corresponds to the resonant-level-scattering model presented in Sec. II. In this model the conduction electrons scatter incoherently from a level of width Γ at an energy E_r away from the Fermi energy with strength S. We also assume the presence of ordinary elastic disorder scattering with rate τ_0^{-1} and plasma frequency ω_p. The parameters used here are given in Table I.

resistivity of 36 $\mu\Omega$ cm, in good agreement with the measured dc resistivity of 41 $\mu\Omega$ cm.

As was mentioned in paper I, Hillebrands et al.[4] have reported a slight increase in the room-temperature ac conductivity of CePd₃ at an energy of about 16 meV, in contrast to the strong decrease in $\sigma(\omega)$ we observe at 4 K. They fitted their data using a memory-function formalism:

$$\sigma(\omega)=\frac{\omega_p^2}{4\pi}\left[\frac{1}{\tau_0}+\frac{A^2}{\Gamma+iE_r-i\omega}-i\omega\right]^{-1}.\quad(9)$$

This form ensures that $\sigma(\omega)$ automatically obeys the Kramers-Kronig relations. In this sense the memory-function approach is similar to (but less complete than) the resonant-level approach. They successfully fitted their room-temperature data using the parameters $E_r=0$, $\Gamma=5$ meV, $A=11$ meV, $1/\tau_0=77$ meV, and $\omega_p=2.15$ eV. The dc conductivity derived from this fit, $\sigma_0=8100$ Ω^{-1}

TABLE I. Parameters of the resonant scattering model fits.

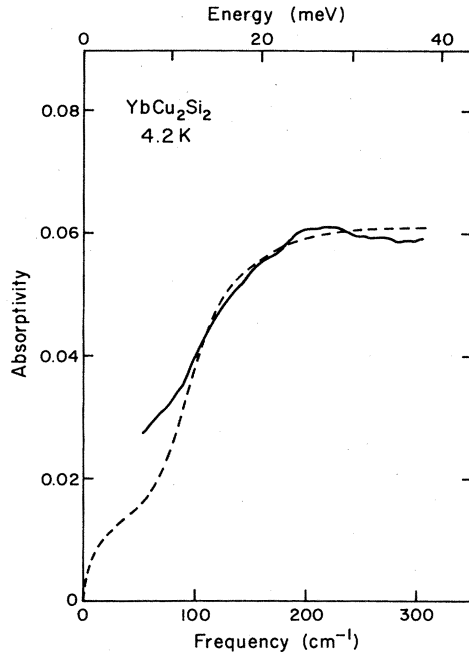| Sample	E_r (meV)	Γ (meV)	S/ω_p^2 (eV^{-1})	$\omega_p^2\tau_0$ (eV)
CePd₃	6.32	1.61	0.0785	890
YbCu₂Si₂	5.58	3.10	0.0254	1430

FIG. 2. Model fit to the absorptivity of $YbCu_2Si_2$ at 4 K. The dashed curve corresponds to the resonant-level-scattering model of Sec. II (see also Fig. 1) using the parameters listed in Table I.

$cm^{-1}(\rho_0 = 123 \ \mu\Omega \ cm)$, is in good agreement with the measured room-temperature resistivity. Because the measurements are done at room temperature, they interpret the assignment $E_r = 0$ as meaning only that $E_r < kT = 26$ meV, consistent with our own assignment. Hillebrands et al. have attempted to use the same formalism to fit our data at 4 K and obtain $E_r = 14$ meV, $\Gamma = 8$ meV, $A = 100$ meV, $1/\tau_0 = 6.6$ meV, and $\omega_p = 2.15$ eV. The fit must be regarded as less successful, however, since the derived resistivity of $\rho = 200 \ \mu\Omega \ cm$ is 5 times greater than the measured resistivity of $41 \ \mu\Omega \ cm$.

By a straightforward extension the absorption anomaly in $YbCu_2Si_2$ at 5 K (see paper I, Fig. 14) can also be described by resonant-level scattering. The best fit (dashed) is shown in Fig. 2 with a set of parameters, listed in Table I, only modestly different from those of $CePd_3$. The resonance occurs at an energy comparable to that in $CePd_3$, but is somewhat broader. We stress again that by symmetry the resonance may be either above or below E_F. The dc resistivity of the model is in this case $48 \ \mu\Omega \ cm$ which should be compared with the experimentally measured value at low temperatures of $7 \ \mu\Omega \ cm$.

III. OPTIC PHONONS

The sharp features at 14.7 and 21.6 meV in the absorption spectrum of $CePd_3$, labeled O_1 and O_3 in Fig. 1, are clearly identified in paper I as zone-center optic-phonon modes. The strength and line shape of these modes were calculated in paper II. An important result from paper II is that the electronic contribution to the dielectric function has a profound impact on the phonon absorption line shape. Specifically, the phonon line shape depends criti-

cally on the ratio $\delta = -x/r$ of the imaginary and real parts of the surface impedance $z = r + ix$ due to the electrons (see paper II, Sec. II D and Fig. 4). In particular, in non-Drude metals (such as $CePd_3$) where $-x/r \neq 1$ in the $\omega\tau \ll 1$ limit it is possible to obtain highly asymmetric absorption lines. This effect will be most important in frequency regions where the absorptivity (and hence r) is changing rapidly, which helps account for the difference in line shapes between O_1 and O_3.

The electronic component in $CePd_3$ is simply given by the ac conductivity $\sigma(\omega)$ describing the absorptivity enhancement. We take $\sigma(\omega)$ from the resonant-level-scattering model [Eq. (5)]. When the optic phonons are included the full dielectric function is given by

$$\epsilon(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega} - \sum_j \frac{\Omega_j^2}{\omega(\omega + i\gamma_j) - \omega_j^2} . \quad (10)$$

The final term encompasses the optic-phonon modes. The frequencies ω_j and widths γ_j are taken from the experiment, while the mode strengths Ω_j are adjusted to fit the observed strengths. The absorptivity is calculated from $\epsilon(\omega)$ using Eq. (8). Figure 3 shows the results of superimposing the optic phonons O_1 and O_3 on the resonant-level fit shown in Fig. 1. In the figure the dotted curve represents the resonant-level model alone prior to the inclusion of the phonon term in Eq. (10). The parameters of the fits are given in Table II, including for comparison the theoretical strength Ω_j calculated in paper II. The calculation reproduces all of the salient features of the data. The details of the strengths and line shapes do not match completely, however, indicating that our understanding of optic phonons in VF materials is incomplete.

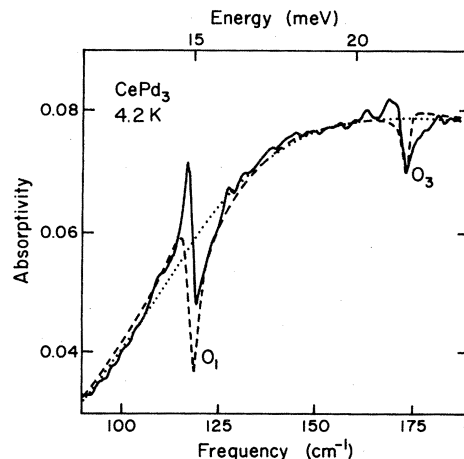Optic phonons exist in metals quite apart from whether

FIG. 3. Absorptivity of $CePd_3$ in the vicinity of the optic-phonon modes O_1 and O_3. The solid curve is the experimental data. The dotted curve is the resonant-level-scattering model fit of Fig. 1 prior to the inclusion of the phonons. The dashed curve is the same resonant-level fit where the optic-phonon modes have been included via Eq. (16). O_1 has center frequency $\omega_1 = 14.6$ meV, width $\gamma_1 = 0.20$ meV, and ion plasma frequency $\Omega_1 = 86.8$ meV.

TABLE II. Optic-phonon parameters in CePd$_3$.

	ω_j (meV)	γ_j (meV)	Ω_j (expt.) (meV)	Ω_j (theor.)[a] (meV)
O_1	14.6	0.20	86.8	68
O_3	21.6	0.20	49.6	20

[a]Reference 2.

or not they are VF materials. We can ask, therefore, whether optic-phonon modes can be observed in the absorptivity of other, particularly non-VF, metals. Although in principle the modes should be observable in other systems, it appears that experimentally the answer is no.[5] Certainly to date they have not been seen in any other compound we have studied, including the isostructural non-VF compound YPd$_3$, whose phonon spectrum should be similar to that of CePd$_3$ (see paper I, Fig. 2). In order to assess the effect of the resonant level on the strength of the optic phonons, we show in Fig. 4 what happens when the resonant level is removed from $\sigma(\omega)$ *while the parameters describing the phonons remain unchanged.* The absorptivity is then that of hypothetical "non-VF CePd$_3$" having the same dc resistivity. The optic phonons, although still present, are barely observable in the spectrum. Indeed, the relative size of the phonon absorption lines decreases much faster than the absorptivity itself. This suggests that while in principle it is possible to observe the optic phonons in any metal, including Drude metals, the absorptivity enhancement in VF materials also enhances the relative magnitude of the optic phonons and renders them more easily observable. In non-VF materials the phonon modes will be most easily observed in "dirty" high-resistivity compounds with a large absorption background.

IV. CONCLUSIONS

We have attributed the broad-absorption anomaly in CePd$_3$ and YbCu$_2$Si$_2$ to resonant scattering of conduction electrons from a level at or near the Fermi level. We place the level within roughly 10 meV of E_F, and with a comparable width. Whether this is correct is far from clear. There are two main schools of thought. One[6] would argue that the f^1 lies 1—2 eV below the Fermi surface and hybridizes so strongly (due to its large orbital degeneracy) with the conduction electrons that a (Kondo?) resonance is produced in the f density of state some tens of meV above the Fermi level. The other[7] point of view proposes a dynamical model in which a "weakly screened" f^1 level lies 1—2 eV below the Fermi level while
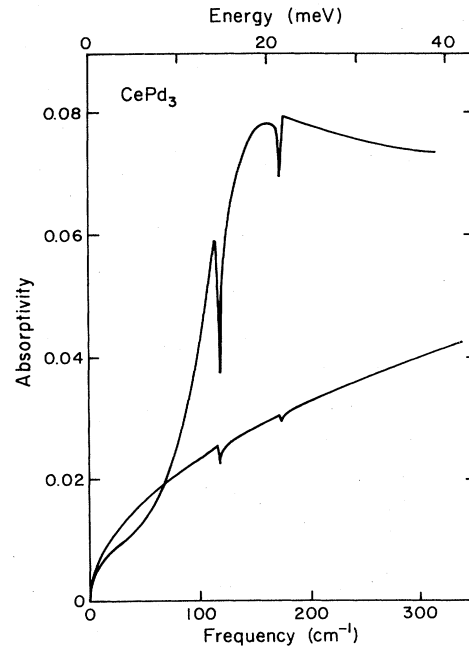

FIG. 4. The relative strength of the optic-phonon modes is sensitive to the magnitude of the absorptivity. The upper curve is the resonant-level fit of Fig. 3 to the measured absorptivity of CePd$_3$, including the optic-phonon modes. The effect of removing the resonant scattering from CePd$_3$ is shown in the lower curve, which corresponds to a hypothetical compound having a Drude frequency dependence and a dc resistivity the same as that of CePd$_3$, 41 $\mu\Omega$ cm. The parameters describing the optic phonons are unchanged. The relative magnitude of the optic phonons is greatly reduced, even though the absorptivity has changed only by about a factor of 2.

a "strongly screened" level lies near but below the Fermi level. In either case there seems evidence for some f-like state near the Fermi level. But what is unclear is the role such an XPS or UPS-detected state would have at far-infrared energies.

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[2]F. E. Pinkerton, A. J. Sievers, J. W. Wilkins, M. B. Maple, and B. C. Sales, in *Valence Fluctuation in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 177; Phys. Rev. Lett. **47**, 1018 (1981).

[3]F. E. Pinkerton, Ph.D. thesis, Cornell University, 1981.

[4]B. Hillebrands, G. Güntherodt, R. Pott, W. König, and A. Brietschwerdt, Solid State Commun. **43**, 891 (1982).

[5]L. J. Sham and J. W. Wilkins, preceding paper, Phys. Rev. B

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[7]This view was originally espoused in a different context by O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **41**, 1608 (1978). For a more recent version applied to Ce, see S. H. Liu and K.-M. Ho, Phys. Rev. B **26**, 7052 (1982).