Optical investigations of the heavy-fermion superconductor UNi$_2$Al$_3$

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The optical properties of the heavy-fermion superconductor UNi$_2$Al$_3$ have been investigated at temperatures between 10 and 300 K using reflectance spectroscopy. A characteristic energy scale ($\omega_c=90$ cm$^{-1}$), with almost the same value as the coherence temperature $T_0=100$ K derived from measurements of the dc resistivity and susceptibility, is obtained from the optical conductivity. At high temperatures ($T>T_0$), this scale represents the energy gap between the ground and excited level that results from the crystal-field splitting of the $5f^2$ ($J=4$) level of the tetravalent uranium ion. In the low-temperature coherent region ($T<T_0$), a narrow, Drude-like, quasiparticle absorption mode develops. This mode is described using a frequency-dependent scattering rate $\Gamma(\omega)$ and mass enhancement factor $\lambda(\omega)$. This free-carrier mode may originate from a hybridization between the 3$d$ conduction band of nickel and the 5$f$ bands of uranium. Parameters such as the renormalized scattering rate $\gamma^*$ and plasma frequency $\omega_p^*$ of the quasiparticle mode, as well as the quasiparticle bandwidth $W$ at 10 K are derived using the model developed by Millis and Lee.

Heavy-fermion materials, especially those that exhibit the coexistence of antiferromagnetic ordering and superconductivity at low temperatures, e.g., URu$_2$Si$_2$ (Ref. 1) and UPt$_3$ (Ref. 2), have aroused a lot of interest among both experimentalists and theorists. In these materials there is usually a characteristic temperature $T_0$, above which spin-disorder scattering of the conduction electrons causes the temperature coefficient of the dc resistivity to be negative; below $T_0$, the scattering is frozen out, resulting in a sharp reduction in resistivity. The temperature dependence of the magnetic susceptibility has a broad peak near $T_0$ that can be explained by crystal-field splitting. Moreover, susceptibility suggests that the 5$f$ moments of the U ions are localized at high temperatures and somehow become delocalized for $T<T_0$. This delocalization has been explained as due to the Kondo effect of the 5$f$ spins being compensated by the spins of the conduction electrons. The trouble with this explanation, as noted by Millis and Lee, is that there are not enough conduction electrons within the range of $T_K$ of the Fermi surface, where $T_K$ is the Kondo temperature, to compensate the spins of the ion. Other authors believe that the orbital moment of the ion is so large in these compounds that it results in an almost compensated 5$f$ orbital and spin moment. The electronic specific-heat coefficient $\gamma_e$, e.g., $\gamma_e=422$ mJ/molK$^2$ for UPt$_3$, suggests an enhancement of the effective mass of the quasiparticles resulting from the many-body effects of the d conduction electrons and the f electrons of U. Attempts to determine the theoretical ground state which accounts for all these unusual and unique properties of the heavy-fermion materials have been made.

Optical reflectance spectroscopy is a very useful technique in the study of these materials because it can probe the electronic excitation spectra of the heavy quasiparticles. The optical properties of the heavy-fermion materials have been studied by reflectance and absorption measurements. Bonn et al. measured the temperature dependence of the reflectance of URu$_2$Si$_2$ in the far-infrared region, finding a spin-density-wave (SDW) gap at the Fermi surface below $T_N$ and a narrow Drude-like mode developing in the coherent region. A similar mode was found in UPt$_3$. Recently, two new heavy-fermion superconductors, UNi$_2$Al$_3$ and UPd$_2$Al$_3$, have been discovered. Both undergo antiferromagnetic as well as superconducting phase transition at low temperatures, with $T_N=4.6$ and 14 K and $T_c=1$ and 2 K, respectively. The crystal structure of UNi$_2$Al$_3$ is of the hexagonal PrNi$_2$Al$_3$ material (space group $P6/mmm$) with $a=5.024$ Å and $c=4.018$ Å and there exists a longitudinal spin density wave with a very small ordered moment $\mu_{ord}=0.24\mu_B$ in the hexagonal basal plane below $T_N$. An optical reflectance measurement has been performed on polycrystalline UPd$_2$Al$_3$, and a zero-frequency narrow resonance at low temperatures was found.

The single crystal of UNi$_2$Al$_3$ used in this measurement was grown at McMaster using the growth process described previously. The crystal quality was characterized using neutron scattering. There are no impurity phases detected. The a-c plane dc resistivity was measured using a four-probe technique. The dc susceptibility was measured by Schroder et al. on a second crystal that was used for neutron scattering measurement. Both measurements yield results that are similar to those reported previously. At high temperatures ($T>150$ K) the resistivity, which is attributed to spin-disorder scattering, saturates, whereas the susceptibility is characteristic of the localized 5$f$ electrons of U. A sharp drop in the resistivity below 100 K is accompanied by a broad
produced to be approximately 100 K.

The spin-disorder from the coherent scattering regions is described by Homes et al. The experimental techniques employed in this work have been described by Homes et al. The details of the UNi$_2$Al$_3$ single crystal have been measured from 300 to 10 K. The temperature reflectance at high frequencies is similar to that of UPd$_2$Al$_3$ and has a bump around 3000 cm$^{-1}$ that also appears at low temperatures. The overall reflectance at high frequencies decreases with decreasing temperature from 300 to 100 K and has little temperature dependence between 100 and 10 K. The temperature dependence of the far-infrared reflectance is shown in Fig. 1(b). Its magnitude decreases with decreasing temperature at higher frequencies, but this behavior changes at lower frequencies below 100 K. The crossover occurs at $\sim$100 cm$^{-1}$ between the 300 and 10 K data, whereas the crossover between 100 and 10 K data occurs at $\sim$150 cm$^{-1}$.

To prepare a UNi$_2$Al$_3$ sample suitable for optical measurements, the single crystal was cut parallel to its $a$-$c$ plane using a spark cutter and was successively polished using the No. 600 diamond grit paper, No. 4000 waterproof silicon carbide paper, 1 μm diamond paste, and finally colloidal alumina solution (0.05 μm Al$_2$O$_3$ powder suspended in water). The temperature dependence of the polarized reflectance of the UNi$_2$Al$_3$ single crystal has been measured from 30 to 8000 cm$^{-1}$ for temperatures between 10 and 300 K using a Michelson interferometer. The temperature-dependent reflectance between 8000 and 44000 cm$^{-1}$ was measured at University of Florida using a grating spectrometer. The details of the experimental techniques employed in this work have been described by Homes et al. We found that the anisotropy of the reflectance between the $a$ and $c$ axes is very small. The results presented here are for the $a$ axis only.

Figure 1(a) shows the reflectance of UNi$_2$Al$_3$ at 300, 100, and 10 K. Generally speaking, the behavior of the reflectance is metallic, decreasing with increasing frequency. The room-temperature reflectance at high frequencies is similar to that of UPd$_2$Al$_3$ and has a bump around 3000 cm$^{-1}$ that also appears at low temperatures. The overall reflectance at high frequencies decreases with decreasing temperature from 300 to 100 K and has little temperature dependence between 100 and 10 K. The temperature dependence of the far-infrared reflectance is shown in Fig. 1(b). Its magnitude decreases with decreasing temperature at higher frequencies, but this behavior changes at lower frequencies below 100 K. The crossover occurs at $\sim$100 cm$^{-1}$ between the 300 and 10 K data, whereas the crossover between 100 and 10 K data occurs at $\sim$150 cm$^{-1}$.

The temperature-dependent reflectance at both low and high frequencies. The Hagen-Rubens relation is used as an extrapolation to low frequencies. The results in the experimental data region do not depend on a specific low-frequency extrapolation used. Between 40000 and 10$^6$ cm$^{-1}$ a power law of $\omega^{-2}$ and, beyond this frequency range, a free-electron-like behavior $\omega^{-4}$ are used. Figure 2(a) displays the real part of the optical conductivity of UNi$_2$Al$_3$ at 300, 100, and 10 K. We discuss first the far-infrared conductivity. Figure 2(b) shows the far-infrared conductivity at 300, 100, and 10 K together with the corresponding values for the dc conductivity. It is noted that the extrapolation of the optical conductivity towards zero frequency agrees with the measured dc conductivity. In all

**FIG. 1.** (a) The polarized reflectance spectra of UNi$_2$Al$_3$ along the $a$ axis at 300, 100, and 10 K in the whole measured frequency region. (b) The far-infrared reflectance of UNi$_2$Al$_3$ at 300, 100, and 10 K. Note that the magnitude of $R(\omega)$ decreases with decreasing temperature at high frequencies, while the opposite behavior is observed at low frequencies below 100 K. The crossover between the 300 and 10 K data occurs at $\sim$100 cm$^{-1}$, whereas the crossover between 100 and 10 K data occurs at $\sim$150 cm$^{-1}$.

**FIG. 2.** (a) The real part of the $a$-axis optical conductivity of UNi$_2$Al$_3$ at 300, 100, and 10 K. The conductivity can be fit to a Drude term and four Lorentz oscillators with the fitting parameters being listed in Table I. (b) The far-infrared conductivity of UNi$_2$Al$_3$ at 300, 100, and 10 K. The values of the dc conductivity of UNi$_2$Al$_3$ at 300 K (square), 100 K (triangle), and 10 K (solid square) as well as a characteristic frequency scale $\omega_c$ ($\sim$90 cm$^{-1}$) are indicated. Note that the conductivity declines for frequency below $\omega_c$ towards its dc value at 300 and 100 K, whereas a narrow Drude-like peak develops for $\omega<\omega_c$ in the 10 K data.
three spectra, there exists a characteristic frequency $\omega_c = 90 \text{ cm}^{-1}$ which divides the conductivity spectrum into two different regions. For $\omega > \omega_c$, the conductivity increases with decreasing frequency, as is typical for metals, and its magnitude is reduced as the temperature is lowered. Below $\omega_c$, the conductivity begins to decline to the dc conductivity value for the 300 and 100 K data, but rises very rapidly to the dc value at 10 K. Note that the characteristic frequency and the characteristic temperature $T_0$, deduced from the dc resistivity and susceptibility, are comparable energies.

To see the far-infrared optical behavior more clearly the real part of the frequency-dependent dielectric function $\varepsilon_1(\omega)$ of UNi$_2$Al$_3$ is shown in Fig. 3(a). At high frequencies $\varepsilon_1(\omega)$ is negative at all temperatures. Below $\sim 100 \text{ cm}^{-1}$ the dielectric function rises dramatically to positive values for the 300 and 100 K curves, but drops sharply at the same frequency at 10 K. We attribute the positive low-frequency $\varepsilon_1(\omega)$ at high temperatures to an interband transition. Recently, Steglich et al.\textsuperscript{20} fit the specific heat to a model that includes a single-site Kondo effect ($S = 1/2$, $T_K = 48 \text{ K}$) and a crystal-field splitting of 125 K ($\sim 90 \text{ cm}^{-1}$) between the doublet of the ground state and the singlet of the first excited state. Also, a gap of $\sim 81 \text{ cm}^{-1}$, which is attributed to the crystal-field splitting, shows up in the tunneling spectrum for $T < T_N$.\textsuperscript{21} The value of this crystal-field gap coincides with the peak of the conductivity at 300 and 100 K, as shown in Fig. 2(b). The large negative values of $\varepsilon_1(\omega)$ in the low-frequency region at 10 K is in accordance with the narrow Drude-like mode shown in the 10 K conductivity spectrum.

Millis and Lee have proposed a theoretical model based on the low-temperature Anderson-lattice Hamiltonian to explain the frequency- and temperature-dependent conductivity.\textsuperscript{6} In this model the total conductivity consists of two components, one describing the impurity scattering and the other describing boson fluctuations. The conductivity for the impurity scattering part is

$$\sigma(\omega) = \frac{(\omega^2_p)^2}{4\pi(\omega^2 + (\gamma^*)^2)},$$

where the renormalized scattering rate $\gamma^* = (m_p/m^*)\Gamma$ ($m_p$, $m^*$, and $\Gamma$ are the band mass, the renormalized mass, and the static scattering rate of the conduction electrons, respectively) and the renormalized plasma frequency $(\omega_p^*)^2 = 4\pi \eta e^2/m^*$ ($\eta$ is the total free carrier density). In this model there is a characteristic frequency $\omega_c = 90 \text{ cm}^{-1}$ for UNi$_2$Al$_3$ above which $\sigma(\omega)$ dies away, causing the conductivity to become independent of frequency at a value of $\sigma_m$. This saturation conductivity $\sigma_m$ is equal to $n_e e^2/(m_p W)$ where $W$ is the quasiparticle bandwidth. Figure 3(b) shows the fit to the 10 K far-infrared conductivity using the formula $\sigma(\omega) = \sigma(\omega) + \sigma_m$ [here, we fit $\sigma(\omega)$ up to 200 cm$^{-1}$]. The parameters obtained from this fit are $\omega_p^* = 3400 \text{ cm}^{-1}$ ($\sim 0.42 \text{ eV}$), $\gamma^* = 25 \text{ cm}^{-1}$ ($\sim 3.1 \text{ meV}$), and $\sigma_m = 3800 \text{ cm}^{-1}$. The dc conductivity, deduced from the parameters of $\omega_p^*$, $\gamma^*$, and $\sigma_m$, is 11 300 $\Omega^{-1}$ cm$^{-1}$ roughly consistent with the measured value of 10 000 $\Omega^{-1}$ cm$^{-1}$. As a check on these parameters, one can estimate the value of $\omega_p^*$ from the superconducting properties using the London-penetration-depth formula in the impurity limit ($\xi < \ll \lambda_I$),\textsuperscript{22}

$$\lambda_p = \lambda_I \left( \frac{\xi}{l} \right)^{1/2} = \frac{c}{\omega_p^*} \left( \frac{\xi}{l} \right)^{1/2},$$

where $\xi$ and $l$ are the coherence length and the mean free path, respectively. Using the measured values of $l = 470 \text{ Å}$, $\xi = 240 \text{ Å}$, and $\lambda_p = 3300 \text{ Å}$ for UNi$_2$Al$_3$,\textsuperscript{20} one obtains $\omega_p^* = 3400 \text{ cm}^{-1}$, in fair agreement with the value that we have obtained in this work.

The development of the narrow Drude-like mode seen in the 10 K data is quite common among the heavy-fermion materials in the coherent region (the region where the spin-disorder scattering is frozen out).\textsuperscript{11,10,19} It is known that the anomalous properties of the heavy-fermion materials are determined by the behavior of the quasiparticles that result from the hybridization between the $d$ conduction electrons and the localized $f$ electrons of U as the temperature is reduced into the coherent region.\textsuperscript{23} The Drude-like mode is governed by the behavior of the quasiparticles, i.e., a large mass and a dramatically reduced scattering at the Fermi level. In studying the optical properties of CrSb, MnSb, NiSb, and NiAs, Allen and Mikkelsen used a generalized Drude formula to get the frequency-dependent scattering rate $\Gamma'(\omega)$ and renormalization factor $\lambda(\omega)$ of these materials.
dependent scattering rate turns up near 100 cm$^{-2}$.

The mass enhancement $m^*/m_e = 1 + \lambda(\omega)$.

The same scheme was used in analyzing the conductivity data of UPt$_3$, URu$_2$Si$_2$, and UNi$_2$Si$_2$ materials as well as the mixed-valence compound CePd$_5$. Here, we use the same formalism to get $\Gamma(\omega)$ and $\lambda(\omega)$ for UNi$_2$Al$_3$. To calculate the absolute values of both quantities one must first determine the value of the bare plasma frequency, $\omega_p$. We estimate $\omega_p = 23\,400\,cm^{-1}$ ($\sim 2.9\,eV$) using the static value of $m^*/m_e$ (=48) (Ref. 20) and the relation $\omega_p/\omega_p(10\,K) = (m^*/m_e)^{1/2}$ assuming that the band mass $m_b = m_e$ and the free carrier density $n_c$ does not change with temperature. Using the relation $\omega_p^2 = 4\pi n_c e^2/m_e$, a free carrier density of $n_c = 6.1 \times 10^{21}\,cm^{-3}$ is obtained for UNi$_2$Al$_3$. This value is less than $n_c = 1.09 \times 10^{22}\,cm^{-3}$ obtained for UPd$_2$Al$_3$.

Figures 4(a) and 4(b) show, respectively, the frequency-dependent scattering rate $\Gamma(\omega)$ and renormalization factor $\lambda(\omega)$ of UNi$_2$Al$_3$ at 300, 100, and 10 K. We use the fitting parameter $\gamma^*(10\,K)$ obtained previously and the static value $m^*/m_e$ (=48) obtained from the specific heat measurement by Steglich et al. to get $\Gamma(\omega) = \{1 + \lambda(\omega)\} \gamma^*(10\,K) = 1200\,cm^{-1}$ at 10 K. The values of $\Gamma(\omega)$ and $\lambda(\omega)$ are indicated in the figures as solid squares and triangles. The value of $\Gamma(\omega)$ at 300 K, roughly estimated as $\sim 5700\,cm^{-1}$, is also shown in Fig. 4(a) as the solid circle using the values of the plasma frequency ($\omega_p = 23\,400\,cm^{-1}$) and the dc conductivity (1600 $\Omega^{-1}\,cm^{-1}$). The scattering rate gently decreases with decreasing frequency and the magnitude increases as the temperature is reduced at high frequencies. Interestingly, $\Gamma(\omega)$ turns up near 100 cm$^{-1}$ towards the high dc value due to the interband transition in the 300 and 100 K data. In contrast, at 10 K, $\Gamma(\omega)$ drops sharply below 150 cm$^{-1}$ towards its dc value. Such a drop has been seen in other heavy-fermion materials. The renormalization factor $\lambda(\omega)$ drops off below 100 cm$^{-1}$ and becomes negative at lower frequencies. This unphysical result is due to the interband transition at 300 and 100 K. In contrast, $\lambda(\omega)$ turns up to its high dc value at 10 K.

The static scattering rate of UNi$_2$Al$_3$ for $T \approx T_0$ is quite large due to the spin disorder scattering of the conduction electrons. $\Gamma(\omega)$ dramatically declines with increasing frequency until $\omega < \omega_c$, after which it slightly increases with frequency. For $T < T_0$, $\Gamma(\omega)$ increases with frequency to its saturated value near $\omega_c$. The narrowing of the Drude-like mode found in the 10 K data is due to a small value of $\Gamma(\omega)$ and a further reduction by a factor $[1 + \lambda(\omega)]^{-1}$.

The quasiparticle bandwidth $W$ is $\sim 2400\,cm^{-1}$ ($\sim 0.30\,eV$) deduced from the relation $\sigma_{ac} = n_c e^2/(m_e W)$. Using the relation $m_e/m^* \sim T_K/W$, where $T_K$ is the Kondo temperature, we get $T_K \approx 72\,K$ in comparison with $T_K = 48\,K$ from the fit to the specific heat result. As Lee et al. pointed out, the quasiparticle band results from the $f$ bands being moved up to the fermion level and, then, being narrowed by the hybridization with the $d$ conduction band.

We now discuss the high-frequency conductivity. As shown in Fig. 2(a), the overall conductivity at high frequencies decreases with increasing temperature. We fit the conductivity spectra at 300, 100, and 10 K to a Drude term and four Lorentz oscillators. The parameters of the Drude term at 300 and 10 K have been given above, and for the 100 K case, we assume that the plasma frequency is the same as the one at 300 K and determine the scattering rate using the values of the dc conductivity ($\sim 2000\,\Omega^{-1}\,cm^{-1}$) and the plasma frequency. The fitting results are listed in Table I. The lowest-frequency Lorentz mode corresponds to the interband transition between the ground and the first excited level that is due to the crystal-field splitting mentioned before. Interestingly, we find that the mode still exists at 10 K with the position shifting to a slightly lower frequency though the narrow Drude-like coherent mode is the dominant one in far infrared at this temperature. Three absorption peaks appear in the high-frequency region at all temperatures: One is around 2700 cm$^{-1}$ while the other two are above 10 000 cm$^{-1}$. All are attributed to interband transitions. Similar high-frequency absorption peaks have been also found in UPd$_2$Al$_3$.

In conclusion, we have investigated the temperature dependence of the optical constants of UNi$_2$Al$_3$ using reflectance spectroscopy. A characteristic frequency scale $\omega_c$ (=90 cm$^{-1}$), which is comparable to the characteristic temperature $T_0$ (=100 K) deduced from dc resistivity and susceptibility measurements, is found in the optical conductivity spectra. At high temperatures ($T \approx T_0$) this scale represents the peak position of the interband transition due to the crystal-field splitting of the tetravalent 5$f^2$ ($J=4$) level of uranium. A narrow Drude-like quasiparticle absorption mode develops below $\omega_c$, at low temperatures on account of the hybridization between the 3$d$ conduction band of nickel and the 5$f^3$ bands of uranium. Using the Millis-Lee model, we are able to obtain the renormalized scattering rate $\gamma^* = 25$.
TABLE I. The parameters used to fit the polarized optical conductivity $\sigma_i(\omega)$ of UNi$_2$Al$_3$ along the $a$ axis at 300, 100, and 10 K. $\gamma_D$ and $\omega_D$ are the scattering rate and plasma frequency of the Drude part and $\omega_i$, $\gamma_i$, and $\omega_i^P$ are the center position, width, and strength of the $i$th Lorentz oscillator. All units are in cm$^{-1}$.

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and the renormalized plasma frequency $\omega_P^R = 3400$ cm$^{-1}$ for this narrow mode at 10 K. The quasiparticle bandwidth is also estimated to be $\sim 0.30$ eV.

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