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Antiferromagnetic conductivity mode in the modified Heusler alloy UNiSn

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We report reflectivity measurements on UNiSn and ThNiSn compounds in the frequency range 10–700 cm^{-1} at temperatures 10–300 K, and 10–45 000 cm^{-1} at room temperature. The results are consistent with the observed semiconductor-to-metal transition in the UNiSn system below the 43-K Néel temperature, and with the semiconducting behavior of the ThNiSn compound. A single phonon line was observed in the ThNiSn system at all temperatures, whereas two lines, at 157 and 175 cm^{-1}, in UNiSn split into four lines below the Néel temperature. At the lowest temperatures, the conductivity of UNiSn shows a mode at 18 cm^{-1} which is attributed to the antiferromagnetic transition.

UNiSn and ThNiSn compounds belong to a group of modified Heusler alloys. These materials are characterized by MgAgAs-type structure, which can be described by four interpenetrating fcc lattices at positions A (0, 0, 0), B ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), C ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), and D ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$), one of which, for example, B, is empty. About a decade ago de Groot *et al.*[1] suggested, as was later confirmed experimentally,[2] that this specific structure may lead to a new class of materials. The members of this new class have the property that there simultaneously exists a semiconducting energy gap between valence and conduction bands for electrons of one spin polarization while there is a partially filled metallic band for electrons of the other spin polarization.

The unusual magnetic and electric properties of the modified Heusler alloys have attracted a lot of interest.[3–7] Special emphasis has been placed on studying the anomalous phase transition in the UNiSn compound. This material shows a semiconductor-to-metal transition which coincides with a type-I antiferromagnetic ordering below the Néel temperature T_N=43 K. In contrast, ThNiSn, although isostructural to UNiSn, does not exhibit antiferromagnetic ordering. When UNiSn is doped with Th, the transition temperature T_N decreases, as found by measurements of resistivity and magnetic susceptibility in $\mathrm{U}_{1-x}\mathrm{Th}_x\mathrm{NiSn}$ ($0< x <1$) alloy systems.[8] Our interest in these compounds was to examine the antiferromagnetic transition using optical reflectance techniques.

The samples in our measurements were prepared by arc melting stoichiometric ratios of the constituents in argon.[3] The melt was then wrapped in tantalum foil and sealed in an evacuated quartz tube. The UNiSn sample was annealed at 800 °C for 210 days and the ThNiSn sample for 21 days at the same temperature. The properties of the modified Heusler alloys depend greatly on the preparation conditions. It has been found[5] that short annealing times (<21 days) and/or insufficiently high annealing temperatures can cause some of the atoms be on the wrong sites. Annealing at or above 800 °C for periods of 7 or more weeks might be necessary to produce well-crystallized systems. X-ray measurements on our samples showed that UNiSn and ThNiSn crystallized in a cubic MgAgAs structure, represented by four fcc lattices, one of them being empty. The lattice constants for UNiSn and ThNiSn were 6.39 Å and 6.54 Å, respectively. The crystal structure of MNiSn (M=U, Th) has one formula unit per primitive cell. The M atom is bounded octahedrally to six Sn atoms and tetrahedrally to four Ni atoms, the Sn atom octahedrally to six M and tetrahedrally to four Ni atoms, and the Ni atom tetrahedrally both to four M and to four Sn atoms.

dc resistivity measurements of the samples were done[3] using a four-probe method (inset, Fig. 1). For UNiSn the resistivity ρ increased initially as the temperature decreased, reaching a maximum around 50 K, and then decreased sharply at lower temperatures. The value of the maximum resistivity was about an order of magnitude higher than expected for a metallic system. In the

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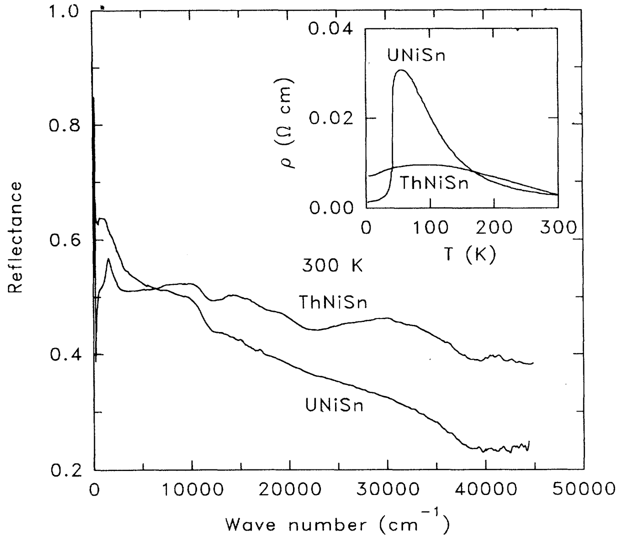

FIG. 1. Room-temperature reflectance from 10 to 45 000 cm^{-1}. Note the suppressed zero. The inset shows the resistivity.

region 100–300 K the resistivity showed an exponential dependence $\rho \sim \exp(E_g/2kT)$, where $E_g = 70$ meV (560 cm^{-1}). According to band-structure calculations[6] the majority-spin band in the UNiSn system becomes metallic at lower temperatures, leading to the dramatic decrease in resistivity below 50 K. The initial increase in resistivity at higher temperatures is due to the semiconducting gap in the minority-spin band. The resistivity of the ThNiSn sample showed a wide peak around 90 K. Above 200 K the resistivity had the same exponential dependence as in the UNiSn system, with a gap value around $E_g = 66$ meV (530 cm^{-1}). The electrical properties of the isostructural UNiSn and ThNiSn systems suggest that the MgAgAs-type crystal structure is responsible for their semiconducting behavior.

Magnetic measurements,[3] together with neutron diffraction measurements,[9] on the UNiSn system show an antiferromagnetic ordering below $T_N \simeq 43$ K. The system is paramagnetic at higher temperatures. A peak in the specific heat $C(T)$, a break in the magnetization curve $M(T)$, and a maximum in $\delta\rho/\delta T$ all occur at 43 K, indicating that a semiconductor-to-metal transition may be correlated with the antiferromagnetic ordering. ThNiSn, in contrast, is a paramagnet at all temperatures. The magnetic properties of UNiSn, which do not occur in ThNiSn, indicate that the anomalous behavior of the uranium compound may be due to the presence of the $5f$ electrons.

We determined the optical properties of UNiSn and ThNiSn through measurements of reflectance. The room-temperature reflectance in the frequency range 650–4000 cm^{-1} was measured by a Nicolet 520 infrared spectrometer equipped with a HgCdTe detector. We used a sputtered gold film of thickness 1500 Å as a reference. From 3800 to 45 000 cm^{-1}, a Perkin-Elmer grating spectrometer was used with aluminum as a reference. In this frequency range two detectors were used: a PbS from 3800 to 18 000 cm^{-1} and a Si photodiode for the rest of the spectrum. Reflectance in the 10–700 cm^{-1} range at temperatures from 10 to 300 K was obtained by Fourier-transform interferometry. The details have been published elsewhere.[10]

Figure 1 shows the room-temperature reflectance of UNiSn and ThNiSn in the frequency range 10–45 000 cm^{-1}. The reflectance approaches unity at low frequencies, indicating the presence of the conduction electrons. The reflectance generally decreases with increasing frequency, with a number of bands seen in the visible and infrared. In particular, there is a sharp peak in the infrared, with a maximum at about 800 cm^{-1} (0.1 eV) in UNiSn and at 1500 cm^{-1} (0.19 eV) in ThNiSn.

Kramers-Kronig[11] transformations were performed on the reflectance data to obtain the optical conductivity, shown in Fig. 2. There is considerable uncertainty at high frequencies in these spectra. This occurs on account of the necessity to extrapolate the reflectivity at frequencies higher than 45 000 cm^{-1}. Although always present in Kramers-Kronig results, the uncertainty is particularly large in the present case for the following reasons. When there is a clear plasmon minimum in the reflectance, the oscillator strength at frequencies below the minimum is well defined by the location of the plasmon frequency and the plateau value of the reflectance above the minimum. Because such a plasmon minimum does not occur here, the low-frequency oscillator strength is highly sensitive to the details of the high-frequency extrapolation. We used a power-law extrapolation $\mathcal{R} \propto \omega^{-s}$ with the exponent s adjustable over 45 000 cm^{-1} -1×10^6 cm^{-1} and $s = 4$ at higher frequencies. This form simulates interband transitions in the ultraviolet region, followed by free-electron behavior. The curves shown in Fig. 2 were obtained with $s = 2$; the overall oscillator strength varied by a factor of 2 as s changed from 0.7 to 3. [For values smaller than 0.7, we got negative regions for $\sigma_1(\omega)$.] Despite these difficulties in the near-infrared–ultraviolet regions, the results

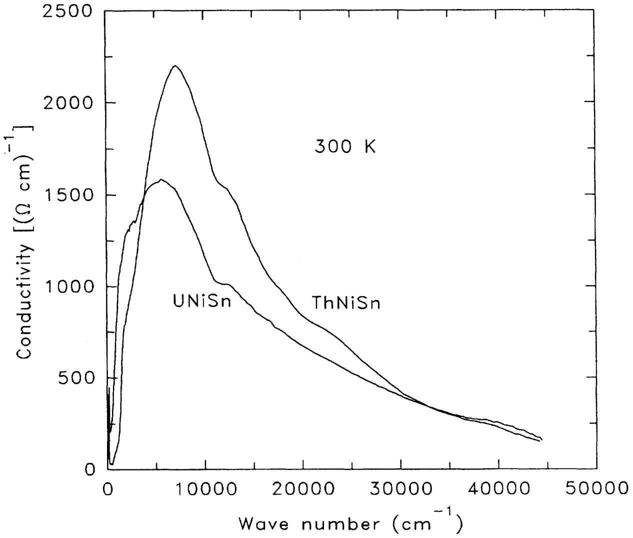

FIG. 2. Real part of the conductivity at room temperature. Both compounds show a semiconducting gap.

were relatively insensitive to extrapolation choice below 4000 cm^{-1} (0.5 eV).

At room temperature both compounds show a conductivity threshold, at ≈ 0.1 eV for UNiSn and 0.2 eV for ThNiSn. Other common features are the presence of interband transitions near 1.1 and 1.9 eV (9000 and 15 000 cm^{-1}). For the Th-based compound there is an additional band around 3 eV (25 000 cm^{-1}).

Assuming that there are three conduction electrons per unit cell and using the free-electron mass, the theoretical contribution of the valence electrons to the sum rule for the U compound is 2.6×10^7 $(\Omega\,\mathrm{cm})^{-1}\,\mathrm{cm}^{-1}$. Our measured value is 3.1×10^7 $(\Omega\,\mathrm{cm})^{-1}\,\mathrm{cm}^{-1}$. For the Th compound the corresponding values are 2.5×10^7 $(\Omega\,\mathrm{cm})^{-1}\,\mathrm{cm}^{-1}$ and 3.8×10^7 $(\Omega\,\mathrm{cm})^{-1}\,\mathrm{cm}^{-1}$.

The temperature dependence of the reflectance of the UNiSn sample above the antiferromagnetic transition temperature in the frequency range 10–700 cm^{-1} is given in Fig. 3. Generally, the reflectance tends towards unity at low frequencies, although this is not unambiguously true at 97 K. The far-infrared reflectance decreases with decreasing temperature, consistent with the decreasing dc conductivity. Two phonon lines are observed at 157 and 175 cm^{-1}. Above about 500 cm^{-1} the reflectance shows a plateau or even increases with frequency. This behavior is particularly noticeable in the temperature range between 137 and 210 K, and is consistent with the presence of a gap for interband transitions around 500 cm^{-1} in accordance with the gap estimate from resistivity measurements.

In the antiferromagnetic state the reflectance shows a number of temperature-dependent features (Fig. 4). At low frequencies the reflectance decreases as the temperature increases. Close to the Néel temperature (the 42-K spectrum), the reflectance is nearly constant at low frequencies, approximately 67% as $\omega \rightarrow 0$, indicating the freezing out of free carriers. In addition to the lines at 157 and 175 cm^{-1}, which are present at all temperatures, two additional phonon lines at 140 and 184 cm^{-1} can be seen. These lines become weaker as the temperature increases and are not present for $T \geq 42$ K; both shift to lower frequencies before becoming unobservable. (See Table I.)

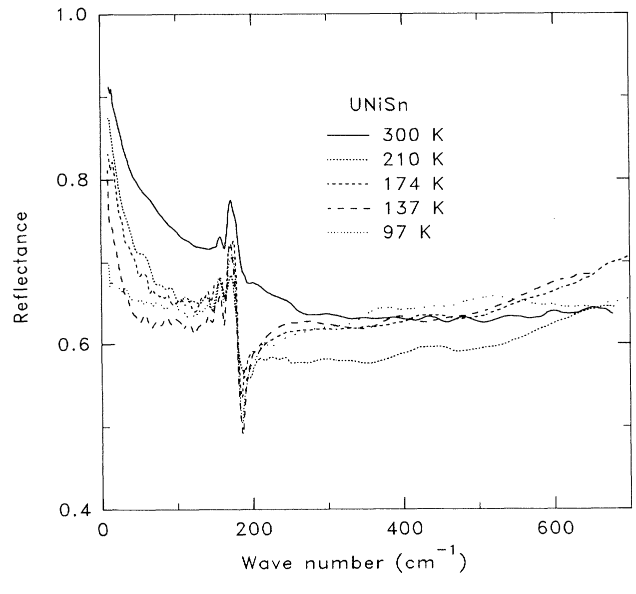

FIG. 3. Reflectance for the UNiSn compound above the antiferromagnetic transition temperature $T_N = 43$ K from 10–700 cm^{-1}.

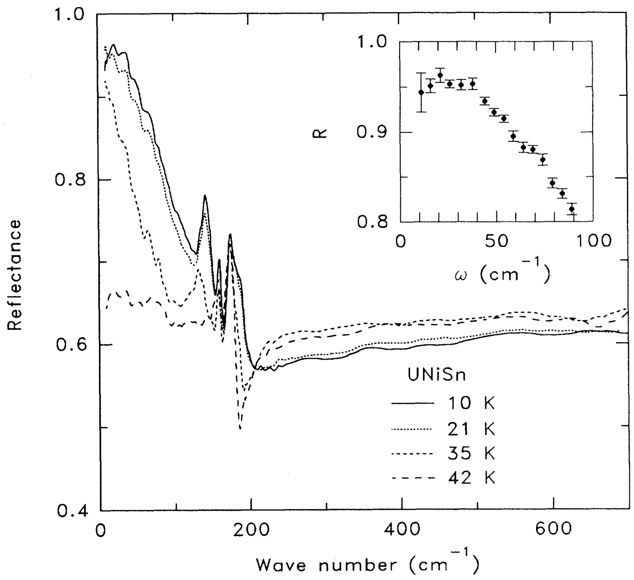

FIG. 4. Reflectance for the UNiSn compound below the antiferromagnetic transition temperature. Inset shows the standard error bars for 10 K obtained by averaging seven spectra.

As shown in the inset to Fig. 1, the resistivity of ThNiSn increases with temperature until about 90 K, has a broad peak between 90 and 200 K, and then decreases at higher temperatures. The reflectance in the frequency range 10–700 cm^{-1}, measured at six temperatures spanning this maximum, is shown in Fig. 5. (There is little observable difference in the reflectance between 8 and 30 K.) As the temperature increases toward 90 K the low-frequency ($\omega < 50$ cm^{-1}) reflectance has very little temperature dependence. Above 200 K, as the dc conductivity increases again, there is a rise in the reflectance below the phonon feature. There is only one phonon line, at 164 cm^{-1}; it shows the expected increase in width with increasing temperature.

At still higher frequencies, above about 450 cm^{-1} (56 meV), the reflectance of ThNiSn is flat at high temperatures, but shows a rising reflectance at lower temperatures, similar to the case of UNiSn. The onset of this rise is close to the value of the semiconducting gap of 66 meV. The magnitude of the reflectance also decreases with increasing temperature, indicating a transfer of oscillator strength from high to low frequencies with increasing temperature.

We fit the reflectance for both samples in the 10–700 cm^{-1} region to a Drude-Lorentz model (Fig. 6). In this model the dielectric function of the system, $\epsilon(\omega)$, is

TABLE I. Drude-Lorentz fitting parameters for UNiSn for $\omega < 700$ cm^{-1}.

	300 K	210 K	174 K	137 K	97 K	51 K	42 K	35 K	21 K	10K
ω_1' (cm^{-1})								135	140	140
γ_1' (cm^{-1})								15	10	10
Ω_1' (cm^{-1})								300	300	315
ω_1 (cm^{-1})	157	157	157	157	157	160	160	160	160	160
γ_1 (cm^{-1})	4	4	4	3	3	1.5	1.5	1.5	1.5	1.5
Ω_1 (cm^{-1})	122	122	122	122	122	100	100	100	100	100
ω_2 (cm^{-1})	174	174	174	175	176	175	175	175	175	175
γ_2 (cm^{-1})	10	10	10	6	6	6	6	6	6	4
Ω_2 (cm^{-1})	387	316	316	332	332	346	346	283	245	187
ω_2' (cm^{-1})								182	184	184
γ_2' (cm^{-1})								10	10	10
Ω_2' (cm^{-1})								200	200	200
ω_p (cm^{-1})	2750	1700	1000	450	450	200	200	1050	1620	1720
$1/\tau$ (cm^{-1})	680	550	275	100	150	150	150	135	180	180
ϵ_∞	85	62	76	76	74	72	72	80	78	78

$$\epsilon(\omega) = \epsilon_\infty + \sum_j \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\gamma_j\omega} - \frac{(\omega_p\tau)^2}{(\omega\tau)(\omega\tau + i)}. \quad (1)$$

The first term in the equation is the limiting high-frequency dielectric constant, here including all the interband transitions above about 400 cm^{-1}. The second term represents the phonon contribution and the third term the Drude contribution. The quantities Ω_j, ω_j, and γ_j are the oscillator strength, the phonon frequency, and the half-width, respectively, while ω_p and τ are the plasma frequency and the scattering rate of the free carriers. The parameters obtained from the fit are given in Tables I (UNiSn) and II (ThNiSn).

The principal result of the fit is that the free-carrier concentration in both compounds is temperature dependent. The plasma frequency, defined by $\omega_p = \sqrt{4\pi ne^2/m^*}$, is a measure of the ratio of carrier concentration to effective mass. The temperature dependence of the free-carrier-density–effective-mass ratio is shown in Fig. 7. For the Th-based system the free carriers freeze out as the temperature decreases, so that at low temperatures the carrier density is only about 20% of that at room temperature. In contrast, for the U system the carriers initially decrease in number as the temperature decreases, reaching a minimum at 50 K of only about 1% of their 300 K concentration before rising again. The concentration at 10 K is about 40% of the 300 K value.

Using a free-electron mass, the estimated carrier con-

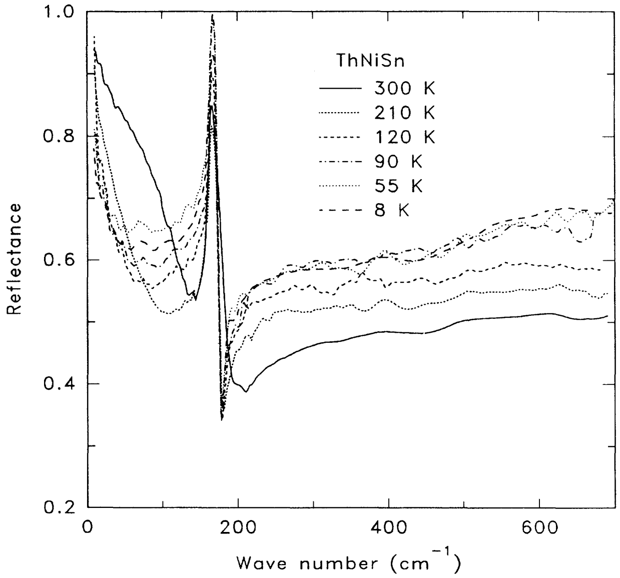

FIG. 5. Reflectance for the ThNiSn compound from 10 to 700 cm^{-1}.

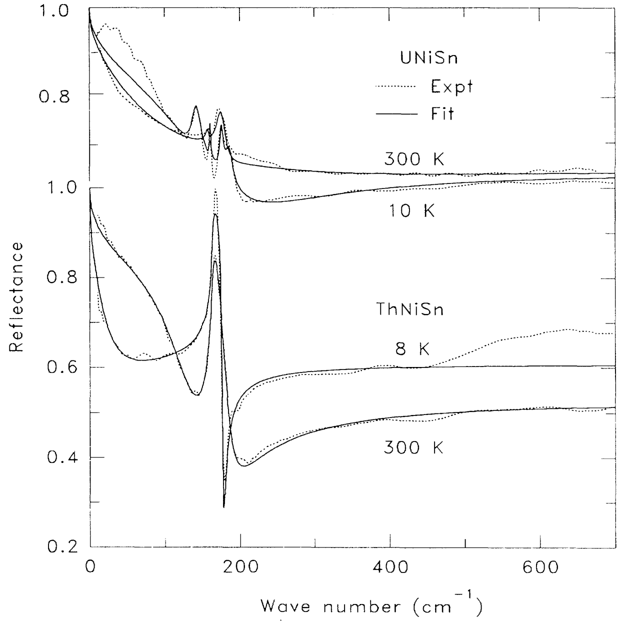

FIG. 6. Representative Drude-Lorentz fit for UNiSn and ThNiSn at two temperatures. The reflectance for ThNiSn below 450 cm^{-1} can be fitted with the Drude-Lorentz function for all the temperatures measured, whereas for UNiSn the reflectance below 100 cm^{-1} at 10 K could not be fitted.

TABLE II. Drude-Lorentz fitting parameters for ThNiSn for $\omega < 700$ cm^{-1}.

	300 K	210 K	120 K	90 K	55 K	30 K	8 K
ω_1 (cm^{-1})	164	164	164	164	164	164	164
γ_1 (cm^{-1})	5	5	3	3	2	2	2
Ω_1 (cm^{-1})	346	360	418	500	566	500	520
ω_p (cm^{-1})	1020	580	450	400	550	430	430
$1/\tau$ (cm^{-1})	100	85	80	65	120	100	100
ϵ_∞	39	43	52.5	62	68	65	65

centrations agree with Hall measurements for UNiSn.[4] However, for this compound the fitted values for ω_p and τ for temperatures below 50 K have greater uncertainty since the fit is not as good (Fig. 6). In particular, the measured low-frequency reflectance is considerably larger than is calculated from the fit; to obtain a good fit another oscillator would have to be included around 18 cm^{-1}. Of course, the Drude model cannot produce a maximum at finite frequencies as is seen in the 10-K data for UNiSn.

Another difference between the data and the Drude-Lorentz model fit is the reflectance rise above 450 cm^{-1} at low temperatures for ThNiSn and the rise above 500 cm^{-1} for UNiSn for temperatures between 97 and 210 K.

Figure 8 shows the low-temperature low-frequency conductivity of UNiSn, calculated by Kramers-Kronig analysis. The following approximations of the reflectance were used. Below 10 cm^{-1} the reflectance was extrapolated using the parameters from the fit, so that it approached unity when $\omega \rightarrow 0$. Above 700 cm^{-1} the room-temperature reflectance was merged with the low-temperature data. Above 45 000 cm^{-1} a power-law extrapolation was used, as described above.

Figure 8 shows a low-frequency peak in the conductivity at 10 K. The strength of this peak decreases as the temperature increases. Note that the peak occurs at energies around 2.3 meV ($\simeq$ 26 K), i.e., on the order of the Néel temperature (43 K). We suggest that the peak is due to pinning of a spin-density-wave (SDW) mode, i.e., to phase oscillations of the antiferromagnetic ordering.[12] A similar conductivity peak, although at higher frequencies, has been observed in chromium which has a Néel temperature of 312 K.[13] However, the peak in Cr has been ascribed to the SDW gap rather than to the pinned mode. Systems which undergo a Peierls transition show similar features (see, e.g., Ref. 14). The assignment to a pinned mode in the case of UNiSn is supported by the small oscillator strength of the feature; in the range 0–100 cm^{-1} there is only 5×10^{-4} of the total spectral weight in the frequency range measured. With increasing temperature, the peak shifts to lower energies and loses intensity. It is not seen above T_N. (The summation in the oscillator strength was done from $\omega = 0$ to 100 cm^{-1}.)

In the temperature range 97–300 K the Drude-Lorentz fit and the Kramers-Kronig analysis give similar results below 450 cm^{-1}. The conductivity spectrum of UNiSn shows a rise around 480 cm^{-1} at all temperatures that are not included in the fit. This increase suggests the existence of a semiconducting gap. A gap feature is also observed in the ThNiSn compound.

As mentioned earlier, we observed two infrared active modes at 157 and 175 cm^{-1} in the uranium system. These modes were present at all temperatures.

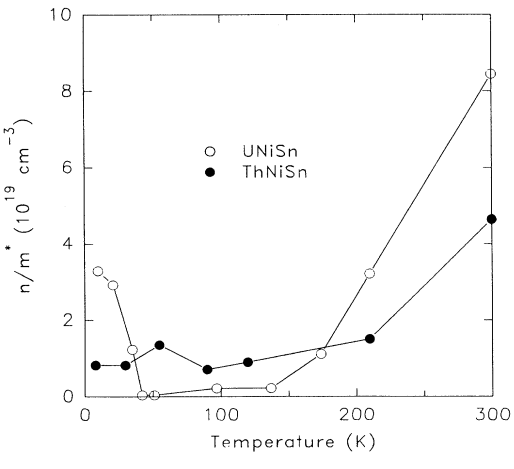

FIG. 7. Carrier-density–effective-mass ratio for UNiSn and ThNiSn as a function of temperature. The lines were drawn as a guide to the eye.

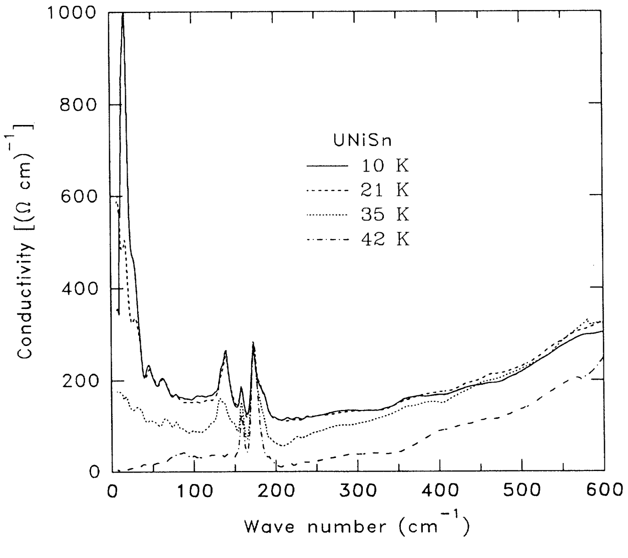

FIG. 8. Real part of the conductivity for UNiSn below 42 K. Note the mode at 18 cm^{-1} which shifts to lower frequencies and weakens as the temperature increases. The measured dc conductivity below 20 K is about 550 $(\Omega\,\mathrm{cm})^{-1}$.

We calculated the frequency of these vibrations using a nearest-neighbor approximation. The lines at 157 and 175 cm^{-1} could be well reproduced by using the following set of force constants: $f_{(\text{Sn-Ni})} = 74\ \text{N m}^{-1}$, $f_{(\text{Sn-U})} = 28\ \text{N m}^{-1}$, and $f_{(\text{Ni-U})} = 13\ \text{N m}^{-1}$. The frequency of 175 cm^{-1} corresponds to the Sn-Ni mode. Although the mass of the U atom also contributes to this frequency, its contribution is not significant because the mass of U is much larger than the mass of Sn or Ni. The mode at 157 cm^{-1} corresponds to the motion of the U atom against Sn and Ni. The presence of two infrared modes in the system with the *M*NiSn crystal structure is predicted by factor-group analysis.[15] Also, room-temperature measurements of far-infrared properties of the *M*NiSn (M=Ti, Zr, Hf) samples[16] revealed the presence of two infrared-active modes in all three samples. The phonon frequencies for these samples were also calculated by using the nearest-neighbor approximation. The obtained force constant between Sn and Ni was slightly larger than for our system, due to smaller distances between the atoms.

Below the Néel temperature two additional modes appear, at 140 and 184 cm^{-1}. By setting the force constants to $f_{(\text{Sn-Ni})} = 68\ \text{N m}^{-1}$, $f_{(\text{Sn-U})} = 29\ \text{N m}^{-1}$, $f_{(\text{Ni-U})} = 15\ \text{N m}^{-1}$, we obtained phonon lines at 183 and 141 cm^{-1}, close to the observed values. However, the room-temperature crystal structure of UNiSn does not allow for four infrared-active modes. The appearance of these two new modes below T_N suggests that there is a doubling of the unit cell in the antiferromagnetic phase. This is consistent with the appearance of a spin-density-wave ground state, as suggested above.

For the Th system, factor-group analysis predicts the existence of two ir modes. However, only one line was observed in our sample. The reason might be that the other line had small oscillator strength, which could not be detected by our apparatus. A presence of one strong and one weak line was also previously observed on some other *M*NiSn samples.[16] A possible explanation for observing only one line in our ThNiSn sample might also be that the two lines are close in frequency so that they overlap. However, if the observed line were indeed the only one present, that might suggest that the sample annealing for longer times might be necessary to achieve correct crystal structure.

In conclusion, we presented the reflectivity spectra of the modified Heusler alloys UNiSn and ThNiSn in the frequency range 10–700 cm^{-1} at temperatures from 10 to 300 K, and the room-temperature reflectivity for frequencies 10–45 000 cm^{-1}. We observed a semiconducting gap for the UNiSn system around 65 meV for temperatures 100–200 K. The ThNiSn sample has a semiconducting gap around 60 meV at temperatures below 90 K. Above the Néel temperature two phonon lines were observed in the uranium system. They split at lower temperatures, suggesting that a lattice change might have occurred. Only one phonon line was observed in the thorium system and is present at all temperatures. Kramers-Kronig calculations and the results of a fit to a Drude-Lorentz model suggest the existence of a spin-density wave for UNiSn at temperatures below 35 K.

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