Optical properties of the vacancy MNiSn lattices (M = Ti, Zr, Hf)

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The optical properties of the intermetallic systems of the type MNiSn (M = Ti, Zr, Hf) have been studied for the first time in the frequency range $100 < \omega < 4000$ cm^{-1} at temperatures $10 < T < 300$ K. An energy gap has been detected at the Fermi level. This gap becomes more pronounced as the temperature is lowered.

A study of the electrical properties of the MNiSn systems (M = Ti, Zr, Hf)[1] and of the UNiSn, UPtSn, and URhSb systems showed that the presence in them of a vacancy sublattice leads to an anomalously low value of the electrical resistivity ρ and to a dependence $\rho(T)$ characteristic of a semiconductor, indicating that a gap can form in the state density near the Fermi energy ϵ_F. Albers *et al.*[3] have recently suggested that a metal-insulator transition occurs in UNiSn as a result of spin splitting of the electron energy by the internal field below the magnetic-transition temperature. In the case of a nonmagnetic intermetallic system MNiSn such an explanation is, however, unacceptable, so that the question of what might cause the appearance of semiconducting properties of MNiSn remains unresolved. Accordingly, we have carried out the first study of the optical properties of the compound ZrNiSn and measured the temperature dependence $\rho(T)$ over the temperature range $300 < T < 1000$ K.

The method of preparation of the samples and the procedure for measuring the electrical properties were described elsewhere.[1] The optical characteristics were measured with the Brucker IFS/113V Fourier spectrometer, equipped with a blow-through optical cryostat operating in the temperature range $5 < T < 300$ K. The crystal structure of MNiSn, which is characterized by a cubic symmetry, consists of four interpenetrating face-centered lattices. The distinguishing feature of MNiSn is the fact that one of the sublattices in it ($C = 1/2; 1/2; 1/2$) is empty in comparison with the intermetallic compounds MNi_2Sn.

Since it was established previously[4] that the nature of the low-temperature properties of MNiSn also depends significantly on the degree of mutual replacement of the atoms in the Zr and Sn sublattices, we studied most thoroughly the optical properties of the compound ZrNiSn N3, which has the lowest degree of disorder ($\sim 10\%$).

To establish the presence of the principal absorption edge and to estimate the magnitude of the optical gap in the range $500 < \omega < 5000$ cm^{-1} at temperatures 300 K, 77 K, and 12 K, we measured the reflection spectra $R(\omega)$ and transmission spectra $T(\omega)$ of a thin ($d \approx 2$ μm) ZrNiSn N3 film (Fig. 1). The frequency dependences of the absorption coefficient $\alpha(\omega)$ (see the inset in Fig. 1) were calculated in the following manner: (a) the fraction A of the absorbed light was determined by means of the

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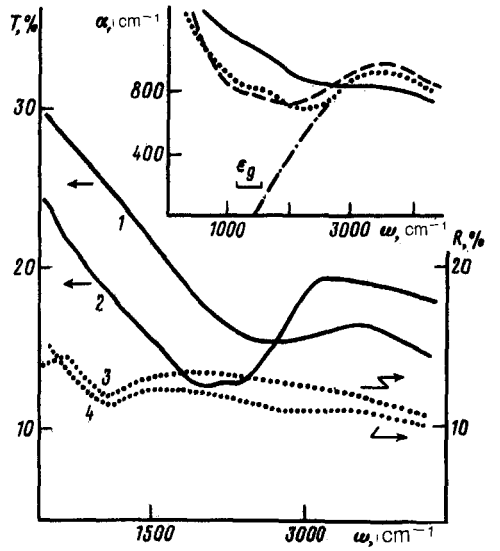

FIG. 1. Frequency dependences of the transition coefficient T (%) and the reflection coefficient R(%) for a thin ZrNiSn N3 film at $T = 300$ K (curves 1 and 3) and at $T \approx 10$ K (curves 2 and 4). The inset shows the calculated dependences $\alpha(\omega)$ for $T = 300$ K (solid curve), T = 77 K (dashed curve), and $T \approx 10$ K (dotted curve).

relation $R(\omega) + T(\omega) + A(\omega) = 1$; (b) the absorption coefficient $\alpha(\omega)$ was calculated in the approximation $A \approx \text{const} \exp(-\alpha d)$.

The minimum on the $\alpha(\omega)$ curve near $\omega \approx 2000$ cm^{-1}, which dips even further with decreasing T, is evidence of the presence of a gap ϵ_g in the electron state density, while an increase in $\alpha(\omega)$ at $\omega < \epsilon_g$ apparently is caused by the free-carrier absorption and by the intraband transitions. The extrapolation of the rf frequency part of the decay of the $\alpha(\omega)$ curve ($T \approx 10$ K) to zero gives the value $\epsilon_g \approx (0.18 \pm 0.03)$ eV. Inaccuracy in the determination of ϵ_g stems from several factors. First, the diffuse reflection of light was ignored in relation (a) since the experiments were carried out with use of polycrystals. Secondly, it should be kept in mind that in the case of degenerate semiconductors the optical measurements give values of ϵ_g that are too high (the Burshtein-Moss effect) and that the calculation of the corresponding correction involves great difficulties. A more accurate estimate of the value of ϵ_g in the limit $T \to 0$ can be obtained by analyzing the $\rho(T)$ curves in the temperature interval $T > 300$ K (see the inset in Fig. 2). By plotting the curves $\ln\rho = f(1/T)$ we found the following estimates on the linear parts in the temperature interval $500 < T < 1000$ K: ϵ_g (ZrNiSn) $\approx 187 \pm 15$ meV, ϵ_g (TiNiSn) $\approx 120 \pm 10$ meV, and ϵ_g (HfNiSn) $\approx 220 \pm 20$ meV. On the basis of $\rho(T)$ measurements Palstra *et al.*,[2] obtained nearly the same value for UNiSn: $\epsilon_g \approx 120$ meV.

The electron and phonon states of MNiSn can be analyzed by measuring the frequency dependences of the reflection coefficient $R(\omega)$ of the ZrNiSn N3 bulk sample (Fig. 2). First, we call attention to the broad minimum of $R(\omega)$, which corresponds to the plasma oscillations, $\omega_{\min} \approx 420$ cm^{-1}. These data, along with the relations in Ref. 5, can be used to estimate the dielectric constant, $\epsilon_\infty \approx 5.8 \pm 0.5$, and the plasma frequency, $\omega_p \approx 380$ cm^{-1}. These data and the results of the Hall measurements,[4] taken collectively allow us to find in the first approximation, the effective mass

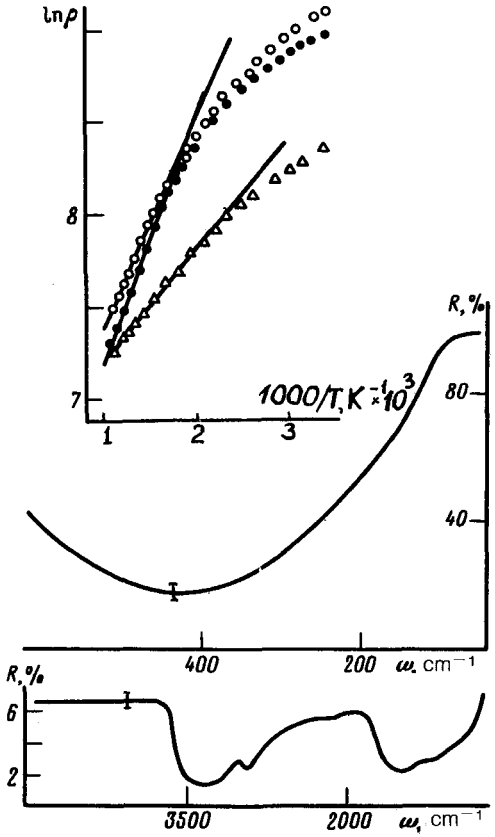

FIG. 2. The reflection coefficient R of bulk ZrNiSn N3 at $T = 77$ K. The inset shows the temperature dependences $\ln\rho = f(1000/T)$ for TiNiSn (△), HfNiSn (●), and ZrNiSn (○).

of ZrNiSn N3: $m^* \approx 2 \pm 0.3\, m_0$, where m_0 is the mass of the free electron. The plasma minimum has also been detected in another sample ZrNiSn N4 with $n_H \approx 7 \times 10^{21}$ cm^{-1} ($\omega_{\min} \approx 1860$ cm^{-1}, $\epsilon_\infty \approx 6 \pm 0.3$; $m^* \approx 4 \pm 0.3 m_0$).

The $R(\omega)$ spectrum has two dips in the frequency range $600 < \omega < 4000$ cm^{-1} (Fig. 2). The low-frequency minimum ($\omega_{\min} \approx 1500$ cm^{-1}) is probably associated with the principal absorption edge and the second minimum ($\omega_{\min} \approx 3500$ cm^{-1}) is most likely associated with the transitions between the valence subbands.

The measurement of $R(\omega)$ of TiNiSn has revealed the presence of a strong anomaly near $\omega \approx 250$ cm^{-1}, whose blurring as a result of raising the temperature from 20 K to 500 K shows that it is linked with the optical phonons.

The optical characteristics which we have obtained confirm, on the whole, that the kinetic properties of the MNiSn system are atypical for the intermetallic compounds. These characteristics also show that the MNiSn system has a gap in the state density near ϵ_F. The most likely cause of the metal-insulator transition of MNiSn may be the asymmetry of the potential of the Zr and Sn atoms, which may lead to the appearance of deep potential wells at the vacancy sites and to the localization in them of the free carriers. A further sharp dip in the minimum of the absorption coefficient

upon lowering the temperature below room temperature (Fig. 1) may be the consequence of the effect of self-trapping on the size and depth of the band gap.

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