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Thermal conductivity of niobium hydrides in the temperature range 4.2–420 K

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Abstract

Measurements of thermal conductivity and electrical resistivity of two niobium hydrides having hydrogen concentrations (H:Nb) of 0.78 and 0.86 were conducted in the temperature range 4.2–420 K. Distinct changes in the temperature dependence of both the thermal conductivity and the electrical resistivity were encountered, obviously connected with phase transitions: $\lambda \rightarrow \beta$ at 200 K and $\beta \rightarrow \alpha' + \beta$ and $\alpha' + \beta \rightarrow \alpha'$ at about 400 K.

Moreover, at about 100 K our results corroborate the existence of a low temperature phase in these compounds. The analysis of the obtained results was conducted on the basis of the models of Wilson and Ziman.

1. Introduction

Investigations of metal–hydrogen compounds revealed that during dissolution in metal, at low concentration of hydrogen, there appears a phase α which is a solid solution of hydrogen in the matrix. Further increase in hydrogen content leads to the appearance of the phase β or several phases, β, γ and δ, which are called hydrides [1]. The phase diagrams of these compounds are rather complicated. On the one hand there appear allotropic modifications; on the other there are phase transitions of the hydrides themselves. The latter can be connected either with rebuilding or deformation of the original lattice or with a change in the way the hydrogen atoms are distributed in the metal lattice [1, 2].

During the last 20 years the results of many investigations of the structural, phonon and electron properties of hydrides of metals of the niobium group have been published [3–5]. However, there have been few works dealing with the transport properties. In refs. 6–8 the electrical resistivity and thermoelectric force of the Nb–H compounds were measured, the anomalies in the course of $\rho(T)$ and $S(T)$ being found at temperatures around 400 K.

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In other studies [8] dealing with $S(T)$ it was found that the transition from the orthorhombic β phase to the cubic α phase causes a distinct change of the thermoelectric force. An investigation of the thermal conductivity of metal hydrides was presented in ref. 9, where the results of measurements of electrical resistivity and thermal conductivity at low temperatures were reported.

The subject of the present paper is the investigation of the thermal conductivity of polycrystalline samples of $NbH_{0.78}$ and $NbH_{0.86}$ in the temperature range 4.2–420 K.

2. Experimental details

The investigated samples of niobium hydride, $NbH_{0.78}$ and $NbH_{0.86}$, were obtained by exposing a niobium single crystal (resistance ratio $\rho_{300}/\rho_{4.2}=56$) to hydrogen gas at a temperature of 850 °C and a pressure of about 5 atm for 2 h. The final content of hydrogen (H:Nb) in the samples was determined from the weight change. Details of the sample preparation method have been given in ref. 7. The samples were cylindrical with dimensions Ø4.5 mm × 20 mm.

The measurements of thermal conductivity were performed by the axial stationary heat flow method in the temperature range 4.2–420 K. The temperature differences in the sample as well as the absolute temperature were determined with a manganin–constantan thermocouple. The average total error in the measured thermal conductivity coefficient κ was about 3%. Because of the rather high temperature of the thermal conductivity measurements (above 300 K) and the very strong influence of thermal radiation, the modified method of thermal conductivity measurement presented in ref. 10 was adopted.

The electrical resistivity of the samples was measured potentiometrically to an accuracy of ±3%. Temperature in the range 4.2–90 K was determined with an (Au+0.03 at.% Fe)–Cu thermocouple, that in the range 90–420 K with a copper–constantan thermocouple to an accuracy of 0.1 K.

3. Results and discussion

Heat is transported by electrons and phonons. The total thermal conductivity coefficient can be written as the sum

$$\kappa=\kappa_e+\kappa_p \tag{1}$$

where κ is the measured value of the thermal conductivity coefficient, κ_e is the electron component of the thermal conductivity and κ_p is the lattice (phonon) component of the thermal conductivity.

Assuming the independence of the resistance processes connected with the scattering of electrons, we may write

$$W_e = \frac{1}{\kappa_e} = W_e^d + W_e^p + W_e^e + W_e^b \tag{2}$$

The two last terms of this expression (the thermal resistance connected with the electron–electron scattering and the electron–sample boundary scattering respectively) can be neglected since they contribute to the total thermal resistance at temperatures below about 1 K only. $W_e^d \propto T^{-1}$ is the thermal resistance caused by the scattering of electrons on physical defects, W_e^p by the scattering of electrons on phonons. W_e^p is the sum of the resistances connected with inelastic scattering of electrons on phonons (proportional to T^2), elastic scattering (proportional to T^4) [11] and "Umklapp" processes (proportional to exp (T^{-1})) [12]. At temperatures lower than 0.1 Θ_D one can write

$$\frac{1}{\kappa_e^p} = W_e^p = \frac{\beta}{T} + \alpha T^2 \tag{3}$$

In metal hydrides, in contrast to pure metals, the phonon term (κ_p) is considerable.

Similarly, we can write for the phonons

$$W_p = \frac{1}{\kappa_p} = W_p^d + W_p^p + W_p^e + W_p^b \tag{4}$$

where $W_p^d \propto T^{n-3}$ is the thermal resistance caused by the scattering of phonons on defects ($n \approx 4$ for point defects, $n \approx 1$ for dislocations), $W_p^e \propto (\Theta_D/T) W_e^p$ is the thermal resistance connected with the scattering of phonons on electrons (W_e^p as above; Θ_D is the Debye temperature), $W_p^p \propto (\Theta_D/T)^3 \exp(\Theta_D/\alpha T)$ is the thermal resistance due to scattering of phonons on phonons (the exponential factor describes the "Umklapp" processes) and $W_p^b \propto T^{-3}$ is the thermal resistance arising from the scattering of phonons on sample boundaries (considerable at temperatures around 1 K).

From the Wiedemann–Franz law and the obtained values of thermal and electrical resistances we have calculated the electron components for the investigated samples. The coefficients in the Wilson equation (3) were determined by the least-squares method. Reasonable agreement (error approximately 1%) has been obtained for temperatures below 60 K.

For $NbH_{0.78}$ the coefficients α and β equal 5.31×10 cm K^2 W^{-1} and 7.77×10^{-4} cm K^{-1} W^{-1} respectively, while for $NbH_{0.86}$ the values $\alpha = 6.48 \times 10$ cm K^2 W^{-1} and $\beta = 1.23 \times 10^{-4}$ cm K^{-1} W^{-1} were obtained. From a comparison of these coefficients one can conclude that in both samples the values of thermal resistance connected with the elastic scattering of electrons on defects are similar. However, $NbH_{0.78}$ has a resistance caused by inelastic electron–phonon scattering almost sixfold greater.

Adding to the right-hand side of eqn. (3) the expression for the resistance governed by the electron–phonon elastic scattering and applying the same method of determining the coefficients, we obtained better agreement (error less than 1%) over a wider range of temperature (up to 100 K).

The equations can thus be written as follows:

$$W^{p}_{e}=5.313\times 10T^{-1}+4.7400\times 10^{-5}T^{2}+1.456\times 10^{-8}T^{4} \quad \text{for } NbH_{0.78}$$

$$W^{p}_{e}=6.490\times 10T^{-1}+0.1063\times 10^{-5}T^{2}+0.966\times 10^{-8}T^{4} \quad \text{for } NbH_{0.86}$$

It should be stressed that the Wilson model describes the results of the experiment with reasonable accuracy only in the region of low temperatures (less than $0.1\Theta_D$).

Using the expression of Klemens [13]

$$n_a=\left(\frac{3.7W^{e}_{p}}{W^{\infty}_{e}}\right)^{1/2}\frac{T}{\Theta_D} \tag{5}$$

the effective number of conductivity electrons per atom has been determined, yielding 0.693 for $NbH_{0.78}$ and 1570 for $NbH_{0.86}$.

The thermal conductivity dependence on temperature in the investigated samples is presented in Fig. 1, together with the so-called recommended curve of $\kappa(T)$ of pure niobium [14]. In the region 200–300 K the values of thermal conductivity coefficient of the investigated samples and of the pure niobium are similar, which may substantiate the notion that in this region heat is transported mostly by free electrons. Niobium hydrides reveal phase transitions when the crystal structure, electrical resistivity, thermoelectric force, sound attenuation and other phenomena are investigated. Figures 2 and 3 present some anomalies of thermal conductivity connected with phase transitions. In the temperature region below 240 K in samples with hydrogen concentration in the range 0.75–0.90 the λ phase exists. On the other hand, at higher hydrogen concentration and below 180 K the γ phase appears

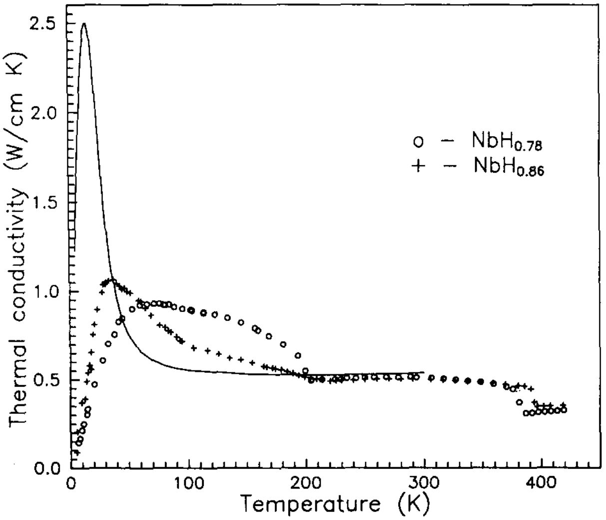

Fig. 1. Temperature dependence of thermal conductivity for $NbH_{0.78}$ and $NbH_{0.86}$. Continuous curve: recommended values of thermal conductivity of niobium [14].

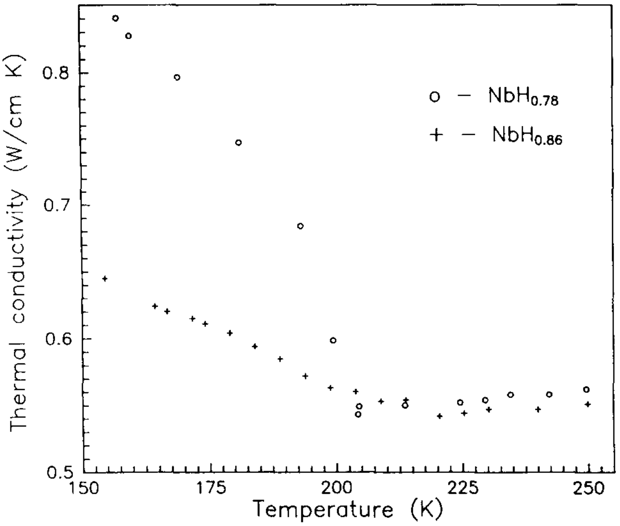

Fig. 2. Thermal conductivity of $NbH_{0.78}$ and $NbH_{0.86}$ in region of phase transitions at about 150 and 250 K.

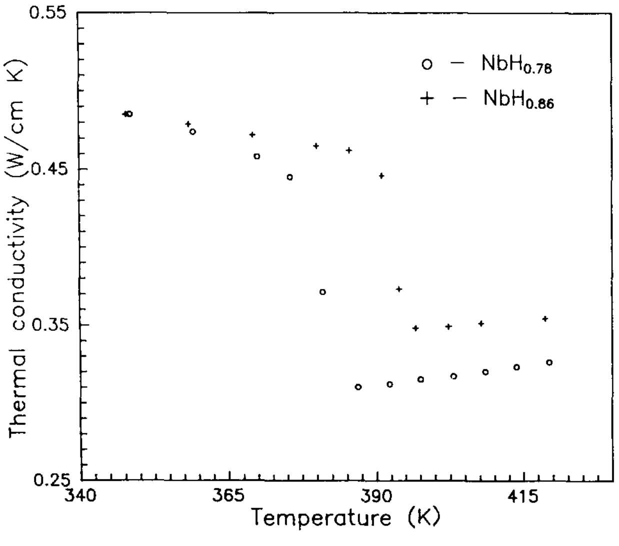

Fig. 3. Thermal conductivity of $NbH_{0.78}$ and $NbH_{0.86}$ in region of phase transitions at about 340 and 415 K.

[15]. These low temperature phases are not yet thoroughly investigated. In Fig. 2 one can see that at about 203 K the decreasing trend of the thermal conductivity changes and the change is greater for $NbH_{0.78}$ than for $NbH_{0.86}$. The character of these changes, as well as the temperature dependence of κ, similar to the recommended curve, indicates a blocking of some dissipative processes, which is connected with the presence of hydrogen in the niobium crystal lattice. Not earlier than about 400 K, owing to phase transitions, the

hydrogen sublattice changes the temperature dependence of the thermal conductivity (see Fig. 3). The decrease in thermal conductivity is visible in NbH$_{0.78}$ at 375 K, which, according to the phase diagrams for Nb–H [1], corresponds to the phase transition from β to $\alpha' + \beta$. Next, at 384 K one can note a distinct increase in κ, which corresponds to the transition $\alpha' + \beta \rightarrow \alpha'$. In NbH$_{0.86}$ the temperature region of the phase transitions is smaller and shifted towards higher temperatures: the transition $\beta \rightarrow \alpha' + \beta$ appears at 392 K and $\alpha' + \beta \rightarrow \alpha'$ at 403 K. Also, the electrical resistivity displays changes connected with the phase transitions at about 200 and 400 K (see Fig. 4).

The phase transitions $\beta \rightarrow \alpha' + \beta$ and $\alpha' + \beta \rightarrow \alpha'$ are transitions of the ordering type [15]. Therefore the transport phenomena, including heat and charge conductivity, are sensitive to these processes and thus easily observable.

The low temperature phase transitions, as was noted earlier, are not well investigated. Nevertheless, considering them in the "ordering" context, one can state that the change in character of the temperature dependence of κ around 200 K indicates a greater degree of ordering in the phase β than in the low temperature phases λ and γ.

Melik-Shakhnazarov *et al.* [15] encountered a series of phase transitions of this kind at about 100 K in their measurements of sound attenuation in niobium hydrides ($0.82 \leqslant \mathrm{H:Nb} \leqslant 0.93$). Also, in our samples a small anomaly in the κ curve is visible at about 100 K. The phonon component of thermal conductivity in pure niobium in the temperature region above 100 K amounts to about 6% [16]. Using the Wiedemann–Franz relation, the percentage contribution of phonons to the heat transport was estimated for NbH$_{0.78}$ and NbH$_{0.86}$. The results are presented in Table 1. The striking difference between the phonon contributions to the thermal conductivity at low temperatures in these samples can be explained through the fact that for the concentrations

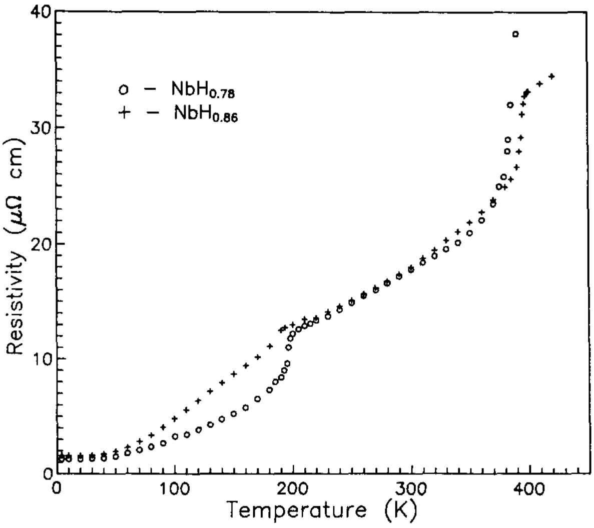

Fig. 4. Temperature dependence of specific resistivity for NbH$_{0.78}$ and NbH$_{0.86}$.

TABLE 1

Percentage contribution of phonons for investigated samples

T (K)	κ_p (%)	
	$NbH_{0.78}$	$NbH_{0.86}$
10	10	58
50	3	39
100	18	28
200	28	25
300	19	19
400	20	20

considered there may arise a process of conduction electron delocalization. This in turn leads to a change in the resistivity originating from electron–phonon scattering. In the region of higher temperatures the phonon–phonon interaction dominates, which causes a linear dependence of the phonon component on temperature and hence leads to the same contribution (19%–20%) of the phonons to the heat transport in both samples of NbH investigated.

In the temperature region 45–200 K it is important to realize that the temperature dependence as well as the value of κ (Fig. 1) and the value of the electrical resistance (Fig. 4) are different for the samples investigated. We see the reason for this difference in the electron–phonon interaction, which in the case of the thermal and electrical conductivity has the character of an Umklapp processes [12]. These are dominant at temperatures above T_{max} (the temperature of maximum thermal conductivity). The Umklapp processes are very sensitive to changes in the Fermi surface topology. Measurements of the thermoelectric power in niobium hydrides [7] indicated that even small changes in hydrogen concentration can considerably change both the Fermi surface shape and the value of the Fermi energy (transfer of electrons from s to d level). Therefore we think that the differences in the $\kappa(T)$ curves in the region $T_{max} < T < 200$ K originate from topology changes.

The lack of a microscopic theory of transport phenomena in metal hydrides and several unresolved problems in this domain, such as the structure of these compounds at low temperatures, forced us to apply simplified models to interpret the results obtained. The importance of these compounds in applications, as well as the wealth of problems in solid state physics, should stimulate more thorough investigation of these hydrides, including thermal conductivity measurements.

References

1 G. Alefeld and J. Völkl, *Hydrogen in Metals,* MIR, Moscow, 1981.

2 H. Wagner, in G. Alefeld and J. Völkl (eds.), *Hydrogen in Metals. I,* Springer, Berlin/Heidelberg, 1978.

3 B. J. Makenas and H. K. Birnbaum, *Acta Metall.*, *30* (1982) 469.
4 M. Gupta, *Phys. Rev. B*, *25* (1982) 1027.
5 H. Metzger, J. Peisl and J. Wanagel, *J. Phys. F: Met. Phys.*, *6* (1976) 2195.
6 N. I. Sorokina, V. V. Evdokimova, I. G. Kuzemskaya, V. Y. Markin, V. I. Savin and A. A. Sobko, *Fiz. Tverd. Tela*, *26* (1984) 969.
7 N. I. Sorokina, *Fiz. Tverd. Tela*, *31* (1989) 123.
8 Z. Henke, O. J. Żogał and B. Staliński, *Solid State Commun.*, *28* (1978) 1009.
9 Š. Melokač, A. Feher, P. Petrovič and Z. Malek, *J. Less-Common Met.*, *118* (1986) 183.
10 A. Ježowski, J. Mucha and G. Pompe, *J. Phys. D: Appl. Phys.*, *20* (1987) 1500.
11 A. H. Wilson, *The Theory of Metals*, Cambridge University Press, Cambridge, 2nd edn., 1954.
12 J. M. Ziman, *Electrons and Phonons*, Clarendon, Oxford, 1960.
13 P. G. Klemens, *Handb. Phys.*, *14* (1956) 198.
14 Y. S. Touloukian and R. W. Powell, *Thermal Conductivity of Metallic Elements and Alloys*, Plenum, New York, 1970.
15 V. A. Melik-Shakhnazarov, I. N. Bydlinskaya, I. A. Naskidashvili, N. L. Arabadjian and R. V. Chachanidze, *Zh. Eksp. Teor. Fiz.*, *81* (1981) 314.
16 F. J. Pinski, W. H. Batler and P. B. Allen, in D. C. Larsen (ed.), *Proc. 16th Conf. on Thermal Conductivity*, Plenum, New York, 1983, p. 155.