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INFLUENCE OF NITROGEN INTERSTITIELS ON THE THERMAL CONDUCTIVITY OF H ON D DOPED SUPERCONDUCTING Nb

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Résumé.- La conductivité thermique de cristaux de niobium contenant H, D, N a été mesurée entre 0,07 K et 1,5 K. Les résultats mettent en évidence la présence de niveaux tunnel de l'hydrogène ou de deutérium piégés sur l'azote en position d'interstitiel.

Abstract.- The thermal conductivity of H, D, N doped Nb crystals has been measured between 0.07 K and 1.5 K. The results show the evidence of tunneling of hydrogen or deuterium trapped by interstitial nitrogen in niobium.

The addition of hydrogen to superconducting Nb produces an isotope dependent specific heat anomaly and resonant phonon scattering at temperatures below 2 K. The latter was interpreted as tunneling of H and D in the Nb lattice /1,2/. Electrical resistivity measurements have shown that the behaviour of hydrogen in Nb is changed considerably by additional interstitials such as N or O providing traps. Since traps are energitically favorable compared to ordinary sites the H and D atoms are attracted to traps at low temperature and do not precipitate as in the case of pure Nb /3/.

The aim of the present measurements of thermalconductivity is to study the influence of N interstitials in H doped Nb. Our thermal conductivity data (temperature range 0.07-1.4 K) were obtained with the standard two heater method using a dilution refrigerator. Wire samples (1.25 mm diameter and 5 cm long) rather than bulk samples were used since they are easy to purify via ohmic heating (2200°C, 10^{10} torr) and can be quenched rapidly enough to prevent nitrogen clustering after doping at 1800°C. The interstitial impurities content (N, O, C) can be reliably controlled by electrical residual resistivity measurements /3/. The samples were doped electrolytically with hydrogen isotopes at room temperature. Since we are only interested in thermal conduction by phonons we have made measurements only below 1.4.K. Below this temperature the contribution of electrons to the heat transport in negligible, due to the high superconducting transition temperature of Nb. To show clearly the phonon scattering, thermal conductivity data are plotted in figures 1, 2, 3 on a reduced scale K/T^3 which is proportionnal to the phonon mean free path l. Its variation therefore can be directly observed.

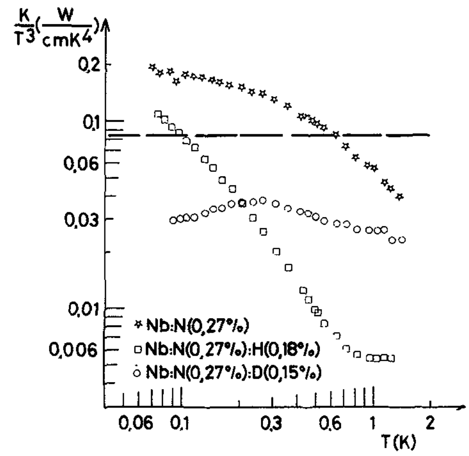

Fig. 1 : K/T^3 versus T experimental points
Nb + N
Nb + N + H
Nb + N + D

The dashed line in figure 1 was calculated assuming a boundary limited l equal to the sample diameter (l = 0.12 cm) with $K = 0.71\ l\ T^3$ ($W\ cm^{-1}\ K^{-1}$) /2/. Data of the N doped sample below 0.1 K are a factor 2 larger than theoretically expected (figure 1). This is not unreasonable if one supposes specular reflections of phonons, since the sample was not abraded. At higher temperatures one observes the influence of N. Due to rapid quenching after doping nitrogen occupies isolated interstitials sites and scatters phonons like a point defect.

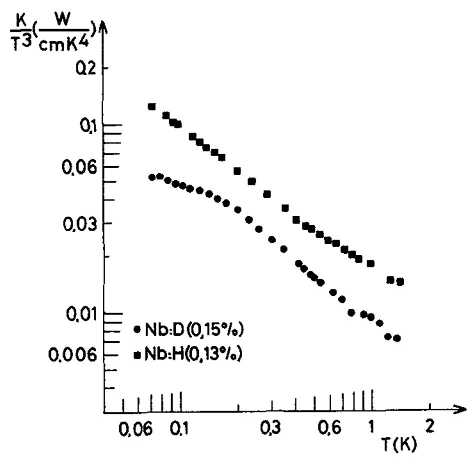

Fig. 2 : K/T^3 versus T experimental points
Nb + H
Nb + D

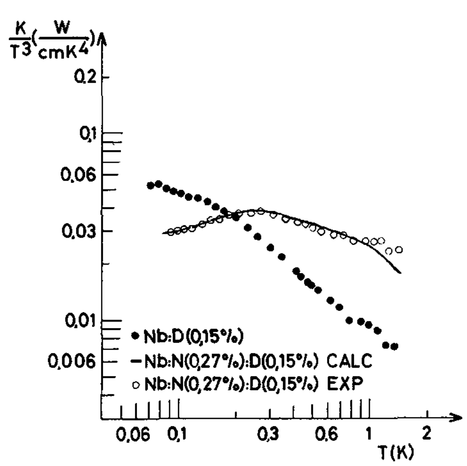

Fig. 3 : K/T^3 versus T experimental points
Nb + N + D with calculated curve
Nb + D

The data of H and D doped sample in figure 2 show a large reduction of 1 but no prononced isotope effect is observed.

According to the Nb-H phase diagram, cooling below 80 K, at slow rates precipitates H or D totally in the β phase hybride. Extended defects like precipitates are strong phonon scatterers, if their size is comparable to the phonon wavelength /4/. A rough estimate gives reasonable values for the size of the precipitates of the order of 50-100 Å. On the other hand a resonance like scattering of thermal phonons due to a dynamic phonon dislocation interactions as it has been proposed by Anderson /5/ can also play a role.

The most striking feature shown in figure 1 is the large isotope effect in samples doped with both N and H or D. Therefore some anomalies below 1 K must be due to H or D trapped on interstitials N in our case. This is particularly clear in the case of D doped samples shown again in figure 3. The high temperature scattering due to precipitates or dislocations, in the only D doped sample disappears nearly completely in the D.N. doped sample.

A quantitative analysis of the thermal conductivity data of doubled doped samples, using the Callaway model, indicates that a least two resonances are necessary to describe the results : one at high frequency (above 1 K) and the other showing the isotope dependence (0.3 K for D and about 0.9 for H). In the case of H, it is somewhat difficult to define the low resonance temperature because the two resonances are not well separated.

The low frequency resonance displaying isotope effect can be explained by a tunneling process of the N - H and H - D pairs. The concentrations in our samples are such that all the H and D are trapped in principle on the N interstitials, so that there are no more precipitates and dislocations /2/ and we can suppose that the resonance at high frequency is also due to same tunnelling energy.

So far we are not aware of a detailed model for the levels of these pairs. The ratio of about 3 between the H and D lowest frequencies cannot be simply explained ; such interstitial pairs are certainly strongly coupled to the Nb lattice and it is therefore not permitted to separate the motion of the N-H pair from that of the surrounding lattice.

Furthermore the concentration of N-H pairs ($\sim 10^{20}$ pairs/cm^3) in our samples is more than an order of magnitude too high to neglect interactions which could impede or prevent tunnelling. We note finally that the small reduction observed at the lowest temperature for the only D doped sample can be attributed to spurious contamination with N, O, C which introduce some pairs.

The presence of residual impurities can also explain the results of Seller et al. who have observed the same kind of thermal conductivity curves as ours. This hypothesis is supported by the fact that the residual resistivity ratio of their samples was only 100 /2/.

In conclusion we have shown evidence of strong coupling of H or D - N pairs with the Nb lattice. Detailed interpretation requires additional measurements on samples with lower N, H concentration, together with a theoretical model for the tunnelling level system.

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