SUPERCONDUCTIVITY OF NIOBIUM AT HIGH PRESSURE

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The influence of all-round pressure on the transition tempera-
ture T_c of Nb is investigated up to pressures of about $25 \cdot 10^3$
kg/cm^2. T_c traverses a flat minimum at about $5 \cdot 10^3$ kg/cm^2 and
rises steeply at higher pressures. The average slope of this
increase is $3.5 \cdot 10^{-5}$ °K cm^2/kg between 10^4 kg/cm^2 and $2 \cdot 10^4$
kg/cm^2.

1. INTRODUCTION

Many new findings have been reported in recent years /1/ on the effect of
mechanical stresses, especially all-round pressure, on the transition tempera-
ture T_c and the critical field H_c of superconductors. A distinct difference
was found between the transition metals and the nontransition metals in the re-
gion of moderate pressures, as has been pointed out by Andres, Olsen, and
Rohrer /2/. With the exception of Tl, the classic superconductors, which be-
long to the group of nontransition metals, exhibit a rather uniform, monotonic
fall of T_c with rising pressure. The transition metals, on the other hand, ex-
hibit a very much smaller pressure effect, which varies greatly, moreover,
from one metal to another.

As substantial deviations from the behavior of the blassic superconductors
had also been observed in the isotope effect in the transition metals, it might
have been assumed that the two phenomena manifested a fundamental difference
between transition and nontransition metals.

To check this conjecture it seems to be necessary to extend the investi-
gations to higher pressures, especially for the transition metals. The example
of Tl, whose transition temperature passes through a flat minimum at moderate
pressures (approx. 1000 kg/cm^2), clearly shows that observations covering a
broader pressure range are needed to establish the presence of any fundamental
differences with any certainty.

The present research was carried out with this in mind. The first sub-
stance chosen was niobium, as no direct observations of the transition temper-
ature under pressure are known. Only the initial rise of the T_c (p) function
could be plotted from measurements of thermal expansion below T_c /3/. It leads
us to expect only a very slight lowering of the transition temperature of nio-
bium as the pressure is raised. Information on the further course of the pres-
sure function of T_c could be obtained only from observations made under pressure.

We measured T_c at pressures up to some $25 \cdot 10^3$ kg/cm^3 to determine this function.

At these high pressures lattice defects are produced by the inevitable plastic deformation that results, and previous observations indicate that this may also affect the transition temperature /4/. To escape this influence of lattice defects, we have to employ a pressure apparatus that enables us to apply and remove the pressure at He temperatures. Traversing the T_c (p) curve several times enables us to effectively separate the irreversible changes due to pressure from the irreversible influences of lattice defects.

2. EXPERIMENTAL

The niobium was procured as wire from the Vakuumschmelze company.* After wires had been rolled out to a thickness of about 0.02 mm, the specimens were cut out, their length being about 2 mm, and their width about 0.2 mm. After this pretreatment the residual resistance ratio R_n/R_{273} approximated 0.05, and the transition temperatures of the specimens lay between 9.4 and 9.5°K. Residual resistance ratios of as little as 10^{-3} could be attained by annealing the rolled out strip in ultrahigh vacuum ($p \approx 10^{-9}$ Torr).

The transition temperature was measured as a function of pressure in a pressure vise, described by Buckel and Gey /5/. This enabled us to apply pressures as high as some $25 \cdot 10^3$ kg/cm^2 at He temperatures repeatedly and then remove them.

The transition to superconductivity was determined by a current-voltage measurement. The measuring current used was 10 milliamps. Varying the measuring current between 5 and 20 milliamps merely shifted the transition temperature, the shift lying within the margin of error in measurement. In order to avoid thermoelectric voltages as much as possible, the voltage taps were connected to the d-c amplifier through a continuous Cu wire. The voltages produced in the annealed specimens of low residual resistance were about 1 microvolt.

Temperature was measured with an Allen & Bradley carbon resistor, whose resistance was 100 ohms at room temperature. It was calibrated at the boiling point and triple point of hydrogen and the boiling point of helium. The requirement that measurement be done in He gas represented a difficulty in the determination of the temperature. Although the thermistor was inserted in a hole in the vise directly adjacent to the pressure cell, appreciable temperature differences between the specimen and the thermistor appeared when the temperature changed rapidly in the cryostat. We therefore established identical conditions within the cryostat prior to each measurement. Moreover, we traversed the transition point as slowly as possible. Under these conditions we were able to measure shifts of the transition temperature exactly down to about 10^{-2} °K.

A dotted-line recorder was used for recording the voltages at the specimen and at the thermistor.

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* It was 99.9% pure.

3. EXPERIMENTAL RESULTS

Some of the transition curves at various pressures are reproduced in Fig. 1. As we were not so much interested in the absolute value of the temperature in these studies, as in its shift under pressure, we have plotted the resistance ratio versus the temperature difference from the uncompressed specimen. At low pressures we clearly see a lowering of the transition temperature, though there are some regions of high T_c. As the pressure is raised, T_c rises; and the transition curves become much broader. Apparently, two effects are responsible for this broadening. On the one hand, inhomogeneities of pressure
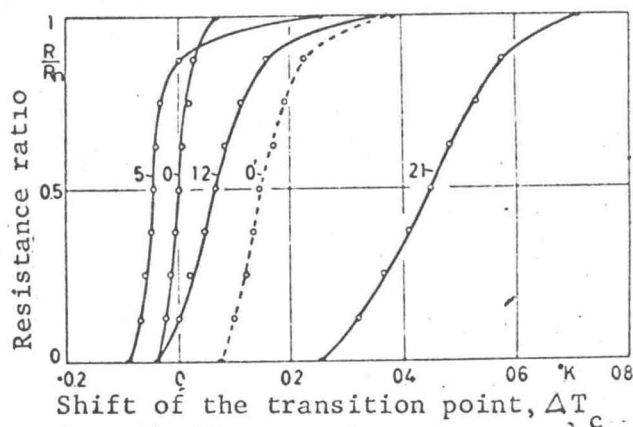

Fig. 1.   Transition curves of Nb under pressure. The figures alongside the curves give the pressure applied in 10^3 kg/cm^2. The dashed curve is observed after the maximum pressure of $21 \cdot 10^{-3}$ kg/cm^2 has been removed. The residual resistance ratio of the initial material is $R_n/R_{273} = 0.05$.

in the concentration of the lattice defects produced by the plastic deformation association with pressure may entail a broadening of the transition curve. The irreversible influence of the lattice defects* becomes apparent after relief of the stress (dashed curve). The transition temperature is raised by the lattice disorder produced. This finding agrees with observations of cold-worked Nb specimens /4/.

The perceptible broadening compared to the original transition curve must no doubt be attributed to inhomogeneities of the lattice defects. On the other hand, this transition curve is much steeper after removal of stress than the curve for $21 \cdot 10^3$ kg/cm^2. Consequently, substantial pressure irregularities may also occur at these high pressures. The regions of high T_c observed at moderate pressures ($5 \cdot 10^3$ kg/cm^2) are probably due to local deformation.

The general shape of the transition curves discussed here appeared more or less distinctly in all the specimens. The transition temperature is shown as a function of pressure in Fig. 2. The plotted points always denote the half-value temperature. The breadth of the transition is plotted for the transition

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* Of course, elastic strains may also be produced during deformation, which remain frozen after relief of stress.

curves shown in Fig. 1 for $0.1 \cdot R_n < R < 0.9 \cdot R_n$. It proved necessary to "shape"
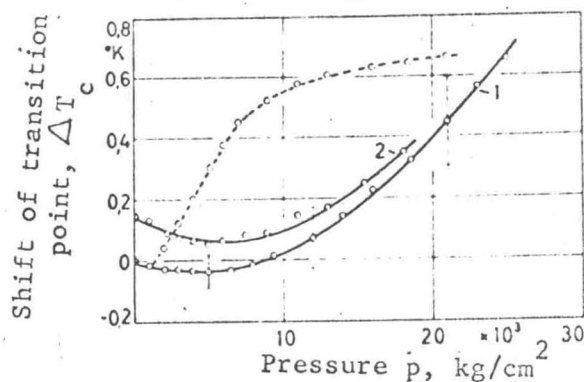

Fig. 2. Transition temperature of niobium specimen versus pressure. The dashed curve was obtained for a pressure cell that was not "shaped." Curve 1 reproduces the function as found in a shaped cell after cooling down from Z.T. Curve 2 can be traversed for the second and subsequent applications of pressure at low temperature.

the pressure cell after assembly, i.e. to subject it to high pressure before chilling. Curve 1 reproduces our observations of a "shaped" pressure cell when pressure was applied after chilling. Pressure was reapplied after stress had been removed, and Curve 2 was found. In both cases T_c passes through a shallow minimum as the pressure is raised.

This relationship was found in all the specimens. When pressure was first applied, without previously shaping the pressure cell, the observations exhibited a quite different relationship. It is plotted in Fig. 2 as the dashed line for the specimen shown there. If we relieve the stress after this "new curve" has been traversed and re-record the T_c (p) function with the pressure cell shaped at the He temperature, we obtain a curve that is almost like Curve 2.

After these two experiments had been completed, we kept the specimen at room temperature for about 24 hours. This annealing apparently reduced the lattice defects enough for the irreversible shift of T_c due to the imperfections to vanish completely. Reapplying pressure at He temperatures then yielded Curves 1 and 2.

The shape of the new curve, which differed from those of all subsequent plots, must be due to very great pressure inhomogeneities that occur during the shaping of the pressure cell. This interpretation is borne out by the fact that the shape of the new curve differed from one specimen to another, which may be due to accidental factors in assembling the minute pressure cell. Moreover, we found extremely broad transition curves in the new curve, which likewise imply the existence of extreme pressure inhomogeneities or great differences in deformation during the initial compression of the cell.

The production of lattice defects by the application of high pressures at low temperatures must also be manifested in the behavior of the residual resistance as a function of pressure. The residual resistance is plotted as

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a function of pressure in Fig. 3 for the measurement whose T_c results are plotted in Fig. 2. We clearly see the irreversible increase in the residual resistance
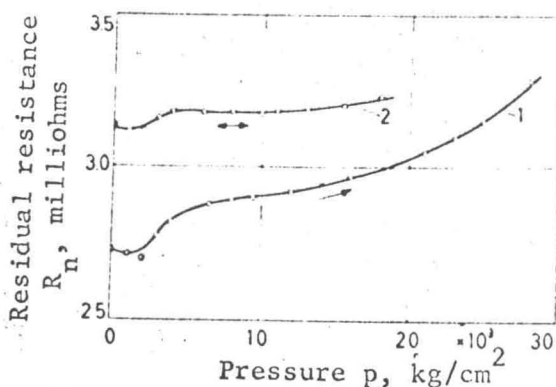

Fig. 3.   Variation of residual resistance with pressure for the specimen shown in Fig. 2.

when pressure is first applied to the specimen annealed at room temperature. The reversible variation of resistance with pressure is very slight. It should be stressed that annealing at room temperature causes the additional irreversible resistance to vanish for the most part.

In order to check whether the observed variation of the transition temperature with pressure is affected in any way by the lattice defects that are responsible for the high residual resistance of unannealed specimens, we also utilized specimens that had been brought up to residual resistance ratios of about $1.5 \cdot 10^{-3}$ by annealing in ultrahigh vacuum.

The results of such a test are shown in Fig. 4. In this case, the shaped cell was chilled, and then a pressure of $25 \cdot 10^3$ kg/cm^2 was applied in one step (solid dot). The load was then removed, and pressure was reapplied, yielding Curve 1. In these specimens as well T_c is raised irreversibly by the initial deformation after chilling. This rise can be eliminated completely by re-annealing at room temperature. After this specimen had stood at room temperature for
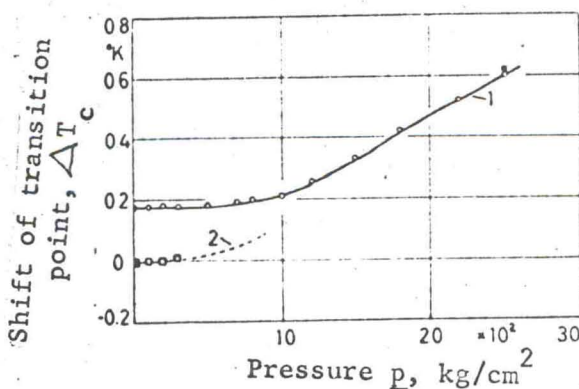

Fig. 4.   Variation with pressure of the transition temperature of an Nb specimen whose residual resistance ratio was small. $R_n/R_{273} = 1.5 \cdot 10^{-3}$.

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three days, its transition temperatures returned to their initial values. At low pressures the variation with pressure exhibits the well-known curve.*

4. DISCUSSION OF RESULTS

The present measurements have confirmed the small initial increase in the T_c (p) function that had been established from observations of thermal expansion. They indicated, however, that at higher pressures (p > approx. $10 \cdot 10^3$ kg/cm^2) the transition temperature is greatly affected in Nb as well. In the $10 \cdot 10^3$ kg/cm^2 to $20 \cdot 10^3$ kg/cm^2 range the mean pressure coefficients for all the Nb specimens investigated** lie between $2.8 \cdot 10^{-5}$ °K cm^2/kg and $4.4 \cdot 10^{-5}$ °K·cm^2/kg, that is, at values whose magnitude do not differ from those observed for the so-called soft superconductors.

The curve of transition temperature versus pressure for Nb is fundamentally different from those of the so-called soft superconductors. The conjecture advanced by Andres, Olsen, and Rohrer /2/ that the transition metals exhibit a special kind of pressure behavior may be fully corroborated in a somewhat extended sense. From this point of view it would appear to be particularly interesting to investigate other transition metals, such as Ta or V, up to higher pressures, in order to learn whether the variation with pressure that has been found in the case of Nb is typical of the transition metals. Köhnlein's measurements /6/ confirm this conjecture.

There is as yet no plausible interpretation of the variation of T_c with pressure discovered for Nb in terms of a microscopic theory. The BCS /Bardeen-Cooper-Schrieffer/ theory yields the following expression for T_c:

$$T_c = 0,85 \cdot \Theta \cdot \exp - (1/N(0) \cdot V),$$

Θ = the Debye cut-off temperature

$N(0)$ = density of states at the Fermi level

V = the interaction parameter of electron-electron interaction

Comparison with the soft superconductors, the lattices of which are not basically different from those of the transition metals, justifies the assumption that the pressure affects T_c essentially via a change in the parameter $N(0) \cdot V$, rather than via a change in Θ.

If the observed variation with pressure is characteristic of the transition metals, a plausible assumption is that the special band structure of the transition metals is an important factor. Whether the observed variation of T_c may be directly ascribed to a shift of the Fermi level toward the vacant bands or much greater changes occur in the density of states when the unit cell becomes smaller must remain a moot question, however.

Further exploration of this problem requires investigation of other transition metals as well as an extension of our experiments to higher pressures, so

* As one electrode broke off, we were unable to cover the entire pressure range.
** 10 Specimens were tested.

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as to learn whether other structures appear in the $T_c(p)$ curve.

If variation with pressure is associated with band structure, we should suppose that appropriate additives, say having different valencies, would change this relationship. Measurements of alloys would be interesting from this point of view. In the present experiments the lattice defects and impurities that we were able to eliminate by annealing in ultrahigh vacuum, had no perceptible effect on the variation of T_c with pressure.

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