Superconducting T_c and Electron-Phonon Coupling in Nb to 132 GPa: Magnetic Susceptibility at Megabar Pressures

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We have measured superconducting T_c using a highly sensitive magnetic susceptibility technique to megabar pressures (>100 GPa). We observed anomalies in $T_c(P)$ for Nb at 5–6 GPa and 60–70 GPa, at which pressure T_c increases by 0.7 K and decreases by about 1 K, respectively. In contrast, T_c in Ta remains nearly constant up to 45 GPa. We suggest that the anomalies in Nb arise from stress-sensitive electronic topological transitions. Between 70 and 132 GPa, T_c for Nb drops continuously to 4.7 K, which is related to the decrease in density of states at the Fermi level with increasing pressure. [S0031-9007(97)04546-8]

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As bcc-structured metals from the fifth row of the periodic table, niobium and tantalum represent textbook examples of *d*-band superconductors for which T_c is generally considered to be well understood theoretically [1]. However, it has been shown that rigid-muffin-tin approximations [2] used in previous calculations of electron-phonon interactions in such metals may not, in general, be justified [3]. Moreover, recent *ab initio* theoretical calculations of the electron-phonon coupling constant in Nb disagree with tunneling experiments [4]. Thus, there is a need for more detailed experimental results and theoretical predictions of the band structure and electron-phonon coupling in Nb. The pressure dependence of T_c is sensitive to the density of states at the Fermi level [1] and, in principle, can be used to investigate the extremal points in the energy bands. At these points, the density of states is peaked and can be moved relative to the Fermi level under the external perturbation of pressure. This approach has been used in early experiments on Tl [5] and Re [6] to pressures of 3 and 2 GPa, respectively, where nonlinearities in $T_c(P)$ were observed that were explained by the creation and destruction of new parts of the Fermi surface as the Fermi level crosses extremal points in the bands. This type of change in Fermi surface topology is widely known as a 2.5 order Lifshitz transition [7].

Previous measurements on Nb and Ta at high pressure have been limited to below 6 GPa [8], which is not sufficient to obtain constraints on different contributions to $T_c(P)$ and the volume dependence of electron-phonon coupling. Moreover, hydrostatic experiments on Nb to 2.4 GPa [9] showed a monotonic decrease in T_c with pressure, while nonhydrostatic measurements to 6 GPa [8] showed a monotonic increase in T_c and an irreversible pressure dependence of T_c. Static compression of Nb to 54 GPa and Ta to 77 GPa and shock-wave experiments on Nb to 170 GPa show no evidence for phase transitions [10,11]. Thus, in Nb any changes in T_c are expected to be related not to the structural changes but to changes in the electronic properties over the measured pressure ranges unless there occur any unknown low-temperature structural transitions.

In this Letter, we extend the range of T_c measurements by magnetic susceptibility to 132 GPa. The measured $T_c(P)$ provides evidence for electronic topological transitions in Nb at 5 GPa and close to 60–70 GPa. In contrast, measurements on Ta to 45 GPa show that such changes are absent in this metal. We also observe a steep decrease of T_c in Nb above 60 GPa, which we explain by the Fermi level moving to the low density of states region after the crossing of *d*-state branches of Γ_{25}' (Γ_8^+) symmetry at the Γ point of the Brillouin zone. Suggested changes in Fermi surface topology in Nb above 60 GPa do not agree quantitatively with theoretical band-structure calculations [12].

We performed the measurements using a highly sensitive magnetic susceptibility technique with diamond anvil cells [13]. Previous magnetic susceptibility measurements have been limited to lower pressures [14,15]. We used a NaCl pressure medium for pressures up to 70 GPa, and no pressure medium for the experiment to 132 GPa. Ruby chips placed in the sample chamber were used as the pressure sensor [16], and pressure was increased at low temperatures. We show representative temperature scans for several pressures in Fig. 1, and the pressure dependence of T_c in Fig. 2. T_c is identified as the temperature where the signal goes to zero on the high-temperature side (Fig. 1) which is the point at which magnetic flux completely enters the sample [13]. $T_c(P)$ is nearly constant in Nb from 10 to 55–70 GPa (depending on the pressure medium used) and from ambient to 45 GPa in Ta (Fig. 2). The 0.7 K increase of T_c in Nb close to 5 GPa is reversible with pressure in a quasihydrostatic medium (NaCl), contrary to the behavior under nonhydrostatic conditions [8]. A related anomaly in dT_c/dP has been observed in NbZr and NbMo alloys [8]. The observed discontinuities in $T_c(P)$ for Nb are similar to observations for Re reported by Chu *et al.* [6], who explained them in terms of an electronic topological

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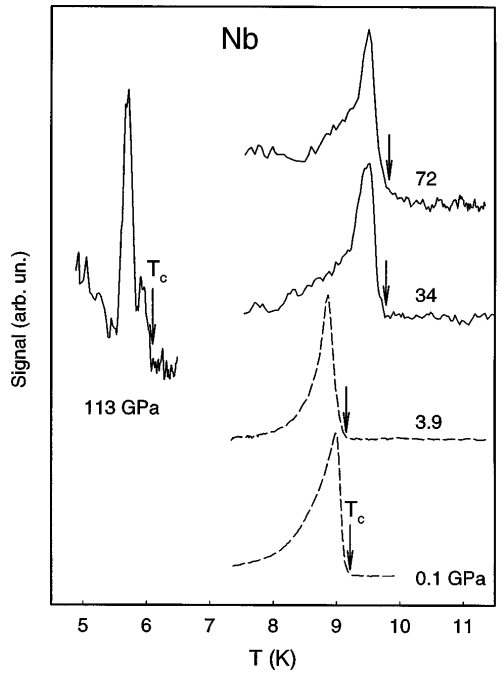

FIG. 1. Experimental data for several pressures, showing the signal from the coil setup and the assignment of T_c. Data at 113 GPa correspond to $60 \times 60 \times 10$ μm sample without pressure medium; lower pressure data are for NaCl pressure medium. Pressures 34 and 72 GPa correspond to $50 \times 60 \times 10$ μm sample; pressures 0.1 and 3.9 GPa correspond to $100 \times 50 \times 10$ μm sample (maximum pressure of 16.6 GPa).

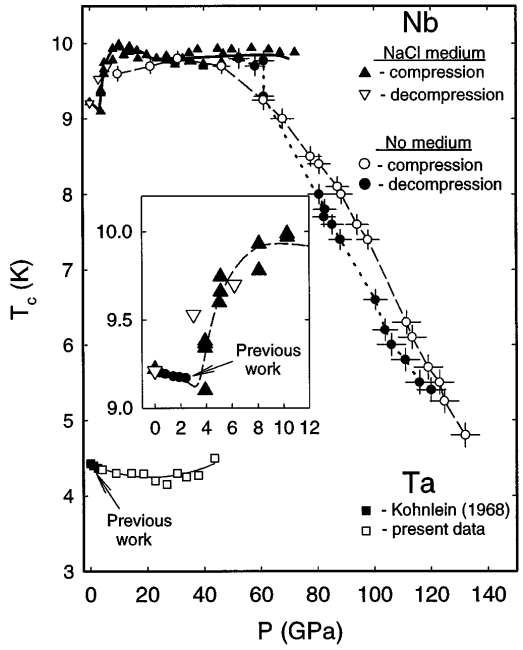

FIG. 2. T_c in Nb to 132 GPa and Ta to 45 GPa. Lines are guides to the eye. Low pressure quasihydrostatic data from Ref. [9] for Nb are shown as closed circles in the inset. Low pressure data for Ta are from Ref. [8].

transition. This (Lifshitz) transition [7] changes T_c by modifying the electronic density of states at the Fermi level, when pieces of the Fermi surface are created or destroyed by pressure. We show below that both the T_c increase at 5 GPa and the decrease at 60–70 GPa in Nb can be explained by changes in topology of the Fermi surface.

We begin by examining the Fermi surface topology of vanadium-group transition metals. Band structure calculations by Mattheiss [17] for Nb and Ta give very similar results, with the Fermi surface consisting of three separate sheets. The second zone Fermi surface sheet has the form of a rather distorted octahedron centered at Γ, and the third zone Fermi surface consists of distorted ellipsoids centered at N and an open sheet extending from Γ to H in the $\langle 100 \rangle$ direction (often referred to as a "jungle gym") (Fig. 3). Calculations of the pressure effect on the Fermi surface of Nb at ~6 and 26 GPa predict no changes in the Fermi surface topology [12,18]. In contrast, calculations for V [19] have shown that a neck between the distorted ellipsoids and the jungle gym is formed along the Γ-N (Σ) direction at about 13.6 GPa. The existence of such a neck implies that the third band along Σ does not cross the Fermi level (Fig. 3). Calculations for V, Nb, and Ta at ambient pressure [20] have this band dipping below the Fermi level by the 14–18, 4–6, and 16 mRy, respectively, for different exchange potentials. Thus, these calculations indicate that in all of these cases such necks do not exist, with Nb being the most likely candidate for them to form under some external perturbation (e.g., pressure). Experimental studies of the Fermi surface of V [21] are reportedly consistent with the existence of necks along Σ even at ambient conditions, whereas these necks are not observed experimentally in Nb [22]. Apparently, experiment and theory do not agree on the Fermi-surface topology in this region of the Brillouin zone. We argue that the anomalies in the $T_c(P)$ in Nb around 5 GPa arise from changes in the Fermi surface topology along Σ, where the third zone (jungle gym) open sheet extending from Γ to H, and ellipsoids (centered at N) touch to form a neck at ambient conditions, which disappears at about 5 GPa [23]. Alternatively, as follows from relativistic augmented plane wave (APW) calculations for Nb [24], it is also possible that the N-H branch of the third band (Fig. 6 in Ref. [24]) also crosses Fermi level only under pressure, and this may be responsible for the disappearance of the neck between ellipsoids and the jungle gym.

To understand the T_c behavior in Nb near 60–70 GPa and above, we estimate the pressure effect on the d bands at Γ_{25}' and N_1' using the results of calculations by Anderson *et al.* [12] for normal and compressed structures (lattice parameter $\Delta a/a = 5\%$ or $P \approx 26$ GPa). The relevant energy bands are shown in Fig. 3. These calculations indicate that the Fermi level approaches the d bands at Γ_{25}' by 1.6 mRy, and the third band at N_1' moves away from the Fermi level by 11.7 mRy when the lattice spacing is decreased by 1%. Thus, at high pressures there is a tendency for the dip near Σ_1 to disappear due to N_1' and Γ_{25}' moving in opposite directions with increasing pressure. Moreover, according to these calculations, the Fermi level

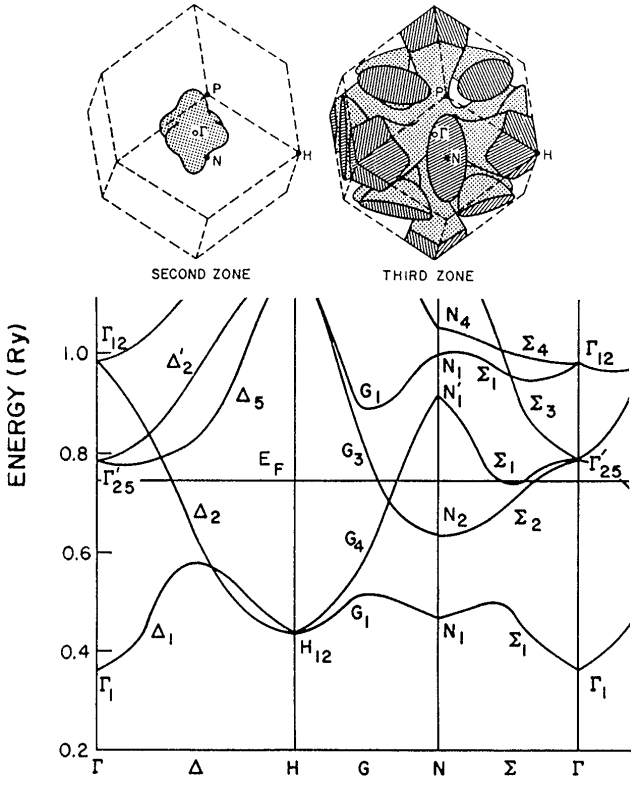

FIG. 3. Fermi-surface model for vanadium-group transition metals after Mattheiss [17] and energy dispersion relations for Nb for normal pressure from nonrelativistic self-consistent APW calculations [12].

crosses Γ_{25}' at about a 30% decrease in the lattice constant (corresponding to pressures above 1 TPa, according to the existing equation of state [11]). Non-muffin-tin potential and spin-orbit splitting of Γ_{25}' into Γ_7^+ and Γ_8^+ branches lower Γ_8^+ by about 20 mRy with respect to Γ_{25}', according to relativistic calculations [24]. Accordingly, a reduction in the lattice constant by 18% is required for the Fermi level to cross the Γ_8^+ branch (still requiring $\sim$300 GPa). We suggest a crossing of the Fermi level with the d bands at Γ_{25}' to occur at 60–70 GPa, which requires a decrease in the lattice constant of about 8%. The decrease of T_c above that pressure is then naturally explained by the Fermi level entering the region with low density of states (see Fig. 3 in Ref. [20]).

However, it is not clear if hydrostatic compression alone produces the suggested changes in Fermi surface topology, because of the existence of uniaxial stresses on the sample at these high pressures, even in a NaCl pressure medium. To estimate the amount of stress and strain in the sample, we first examine the case of Nb placed inside the gasket hole without a pressure medium. We estimate the stress and strain tensors in the sample using the following considerations. The stress distribution in such a gasketed anvil is determined largely by the yield strength σ_y [25–27], which is related to shear strength τ_y by the maximum shear or von Mises yield criterion $\sigma_{33} - \sigma_{11} = t \leq 2\tau_y = \sigma_y$, where σ_{ij} are the components of a stress tensor. The yield strength can be estimated from the pressure distribution over the sample using relation $h(d\sigma_p/dr) \leq \sigma_y$, where h is the sample thickness and $\sigma_p(r)$ is the pressure distribution, and the equality holds if the sample continues to flow [28]. From the equation of state of Nb and the initial thickness of the gasket (16 μm), we estimate the gasket thickness at 60 GPa to be $\sim$10 μm. The measured $d\sigma_p/dr$ was about 0.2 GPa μm at 60 GPa, which gives $\sigma_y = 2$ GPa.

We estimated the deviatoric strain tensor at 10 GPa using the elastic constants for Nb at ambient pressure [30]; for σ_y we interpolated linearly between the ambient pressure ($\sigma_y = 1.1$ GPa) [31], and our calculated value at 60 GPa (10 K) to obtain $\sigma_y = 1.25$ GPa. From this analysis, we expect the uniaxial strain in the sample to be of the order of 0.5%. The hydrostatic part of the strain is about 2% at 10 GPa and about 7.5% at 60 GPa. Thus, not only the pressure distribution in the sample but also uniaxial stresses may produce significant effects on the observed anomalies in T_c. This conclusion is supported by the experimental results shown in Fig. 2. For example, uniaxial strain is expected to have a different effect on the 12 necks in the Σ direction at 5 GPa, due to the different (random) orientations of principal axes in the polycrystalline sample. Thus, in general, the topological transition will be smeared by nonhydrostatic components of the stress (all twelve Σ directions become inequivalent and the topological transition occurs at different mean pressures). Similar considerations apply to the change at 60 GPa, the only difference being that random strain will lift the degeneracy of d bands at Γ_{25}' [32].

We also estimated the electron-phonon coupling constant

$$\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle} \tag{1}$$

using Allen-Dynes [33] modified McMillan's [1] expression for T_c:

$$T_c = \frac{\omega_{\log}}{1.2}\exp\left(\frac{-1.05(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right). \tag{2}$$

We estimated the pressure dependence $\omega_{\log}$ using a pressure varying Slater-Grüneisen parameter

$$\gamma_S = -\frac{1}{6} - \frac{d\ln(K)}{d\ln(V)}. \tag{3}$$

We used a Vinet equation of state with $K_0 = 171$ GPa, $K_0' = 3.6$ for Nb [11] and $K_0 = 194$ GPa, $K_0' = 3.8$ for Ta [34] to estimate $\gamma_S(P)$. Ambient pressures $\omega_{\log}$ for Nb and Ta, as well as the Coulomb pseudopotential $\mu^* = 0.21$ for Nb and $\mu^* = 0.17$ for Ta [35], were taken from Ref. [4]. A significant decrease at high compression and discontinuities at suggested topological transitions are observed in λ of Nb (Fig. 4). In contrast, λ of Ta shows a monotonic decrease with compression.

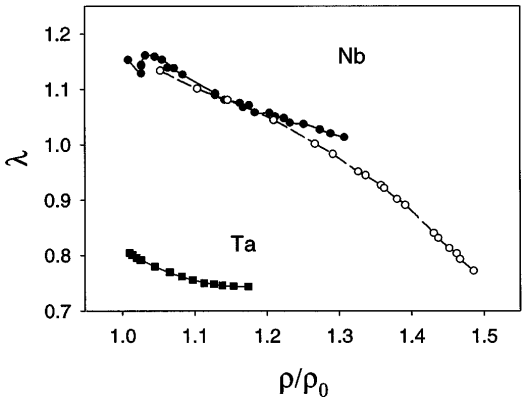

FIG. 4. Estimated density dependence of electron-phonon coupling parameter in Nb and Ta. Lines are guides to the eye. Open symbols for Nb are for the sample without pressure medium; decompression points are not included (see text).

In summary, we have measured the $T_c(P)$ of Nb up to 132 GPa and found evidence for changes in topology of the Fermi surface at 5 GPa and 60–70 GPa. The first is induced by volumetric compression, whereas the second arises from volumetric compression plus a uniaxial strain. Although previous theoretical calculations are, in general, in qualitative agreement with the experimental results, there appear to be significant quantitative differences. In contrast, we observed a flat $T_c(P)$ dependence to 45 GPa in Ta consistent with theoretical predictions for the behavior of the energy bands for this and related metals. More generally, we have demonstrated that measurements of the pressure dependence of T_c can now be performed at megabar pressures (>100 GPa) using magnetic susceptibility techniques. Such experimental data on $T_c(P)$ in this newly accessible range should provide a crucial test of theories of metals under extreme conditions.

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