PHYSICAL REVIEW B VOLUME 58, NUMBER 10 1 SEPTEMBER 1998-II

Reversible depression in the T_c of thin Nb films due to enhanced hydrogen adsorption

N. M. Jisrawi,* M. W. Ruckman, T. R. Thurston,† G. Reisfeld, M. Weinert, and M. Strongin
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000

M. Gurvitch
Department of Physics, SUNY at Stony Brook, Stony Brook, New York 11794-3800

(Received 29 August 1997)

The effect of large hydrogen concentrations (≈30% atomic), on the superconducting transition temperature T_c of Nb films is discussed. The hydrogen is incorporated in solutionlike phases which occur at these concentrations because the (α to β) hydride transition in these films is suppressed. X-ray-diffraction data show an asymmetric expansion of the [110] Nb interplanar spacing. This can be as high as a 6–8 % expansion perpendicular to the plane of the film for the addition of ~70% hydrogen, with only a 1–2 % change in the plane of the film. T_c is depressed to a value near 50% of that of the undoped film with about 30% atomic hydrogen, and returns to its initial value when the hydrogen is removed. A discussion is given of how both disorder and changes in the electronic structure can affect T_c.

[S0163-1829(98)02833-1]

I. INTRODUCTION

The depression of the superconducting transition temperature (T_c) in $A15$ and transition-metal superconductors has been a subject of active interest for decades.[1–4] In these experiments T_c was depressed by introducing disorder into the superconductor through radiation damage[3] or by cryogenic deposition[1,2] and T_c was studied as a function of the residual sample resistivity ρ_0. Alternatively, the sample sheet resistance could be increased gradually by decreasing the film thickness and the effect of weak localization was investigated.[5] However, in general, the great sensitivity of T_c to disorder has never been totally understood, both for transition metals and nontransition metals.

In the present work, we depress the superconducting transition temperature of Nb films with interstitial hydrogen. In this case, T_c is reversibly changed as a function of the hydrogen concentration: it is lowered as hydrogen enters the film and increased as the hydrogen leaves the film. This method constitutes a departure from the irreversible nature of radiation-induced disorder. It will be shown that to understand superconductivity in this system we must understand both the effect of disorder, as well as the change in the electronic states.

Previous investigations of the effect of hydrogen on the superconducting properties of Nb, were hindered by the inability to dissolve more than 1 at. % hydrogen without the precipitation of a nonsuperconducting hydride phase. Therefore, little or no effect on T_c was observed.[6] On the other hand, some work has been done on H in Nb/Ta multilayers[7] and large depressions in T_c were found. In these experiments the individual layer thickness was 20 or 85 Å and proximity effects are a complication in understanding T_c changes. In the present experiments on films about 600 Å thick, we estimate there is up to 30% hydrogen in solution, and this can be increased to 70%. In this case there can be as much as a 6–8 % increase in the interplanar spacing in the direction ⊥ to the plane of the film. For more than 30% hydrogen, T_c is below our lowest attainable temperature of ~4.2 K.

By making the Nb films on the order of 600 to 800 Å, and covering them with a thin layer of Pd, it is found that large amounts of hydrogen can be dissolved in Nb at pressures in the 1 Torr range.[8,9] The Pd keeps the Nb from oxidizing and also has a large effect on the rate at which hydrogen can enter the Nb.[8] Furthermore, it is found that in thin layers the hydride phase is suppressed,[9,10] probably due to the clamping of the film to the substrate, and this accounts for the large amounts of hydrogen that can be absorbed in the layer without hydride formation and ultimately film disintegration.

After a description of some of the relevant experimental conditions, we discuss measurements of the resistivity which is used to estimate the degree of disorder. X-ray measurements are used to establish the two-phase nature of hydrogen in these films and is also used to measure the amount of hydrogen from previous calibrations. A discussion of the proximity effect is used to discuss the nature of superconductivity in this two-phase system and finally a calculation of the density of states is given to show that besides increasing the resistivity through disorder, the hydrogen also reduces $N(0)$. A discussion section then addresses how the reduction in T_c can be understood in terms of both disorder and the decrease in $N(0)$.

II. EXPERIMENTAL

Samples for this experiment were made by dc magnetron sputtering in an argon atmosphere at a pressure of about 8 mTorr. The argon purity was about 1 part in 10^5 and the ambient pressure was about 2×10^{-7} Torr at a pumping speed of about 30 liters/s (the pumping speed during sputtering). The highest measured T_c for films prepared this way was about 8.8 K for an 800-Å film. This transition temperature, which is about 0.5 K below the T_c of bulk Nb, indicates an impurity concentration possibly on the order of about 0.5%.[6] Thinner films show a somewhat depressed T_c due to the proximity effect of the Pd layer.

The films studied here were usually 600–800 Å of Nb on a glass substrate. Even though the 800 Å film is not the optimum thickness for hydrogen uptake without hydride formation, it was necessary to make the film thick enough to reduce the proximity effect from the Pd layer. Several films were 600 Å thick and had a T_c without hydrogen of about 8 K. Since the thickness of the Pd layer is usually small compared to the Nb thickness, its effect on the resistivity is relatively small. Considering the smaller value of the temperature-dependent part of the resistivity, $\approx 10\ \mu\Omega$ cm compared to 14 $\mu\Omega$ cm for Nb, the expected Pd resistance is about five times higher than the Nb resistance. In fact, careful analysis of the effect of the Pd layer thickness on the measured resistance ratios for fully charged and completely uncharged films shows that for 100 Å Pd on 800 Å Nb one needs a correction factor of 0.8 and 0.9, respectively, to obtain the resistance ratios for niobium from those of the measured values for the composite film. Hence, the cover layer is a relatively small contribution to the film resistivity that can be accounted for.

The film's T_c was determined by a dc four-probe measurement with the temperature determined by a calibrated carbon resistor with sensitivity of ±0.1 K in the temperature range 4–20 K. The films were charged with hydrogen *ex situ* in an atmosphere of 15 Torr or higher.

The structure of the films before, during, and after hydrogen charging was determined by x-ray diffraction and more detailed x-ray scattering studies of the anisotropic expansion due to hydrogen uptake were made at the National Synchrotron Light Source (NSLS). The films usually grow with the [110] plane parallel to the substrate, and are most likely composed of grains of the order of 100 Å in size as determined from x-ray line broadening. The lattice expansion with hydrogen was almost entirely in the [110] direction, normal to the film surface. Little expansion was observed in the in-plane direction. In fact, it is the "clamping" of the film to the substrate that plays a role in the anomalous hydrogen sorption properties and unusual phase equilibria.

III. RESULTS

In Fig. 1(a) we show the resistive transitions for a typical 600-Å film at various hydrogen concentrations. The T_c decreases slowly from about 8.0 K for the uncharged film to less than 4 K for a hydrogen concentration of about 60 at. %. The residual resistance at 10 K, ρ_0, without hydrogen is comparable to the change in resistance from 300 to about 10 K. If we assume the temperature-dependent part of the resistance is approximately the same as the room-temperature "handbook" value of 14 $\mu\Omega$ cm, this allows an estimate of ρ_0. Note we are basically assuming an approximation that far from saturation, Matthiesen's rule holds. A further discussion of the temperature dependence as ρ_0 increases is given below. Note, that for an increase of ρ_0 of 50% due to hydrogen, T_c drops to less than 5 K. The single transition for this type of sample is contrasted with the double transition behavior for thicker films shown in Fig. 1(b). Both types of behavior are understood in the framework of a proximity effect model[11] which takes into consideration the particle size in a mixture of two coexisting phases, one with a low T_c and the other with a higher T_c. It should be mentioned that the change in residual resistance is not nearly proportional to the concentration of hydrogen. Initially, at low concentrations, the resistivity changes at a rate of about 0.6 $\mu\Omega$ cm/at. % hydrogen.[12] However, at higher concentrations the volumetric measurements that we have made[10] show a leveling off of the resistivity with the concentration of hy-

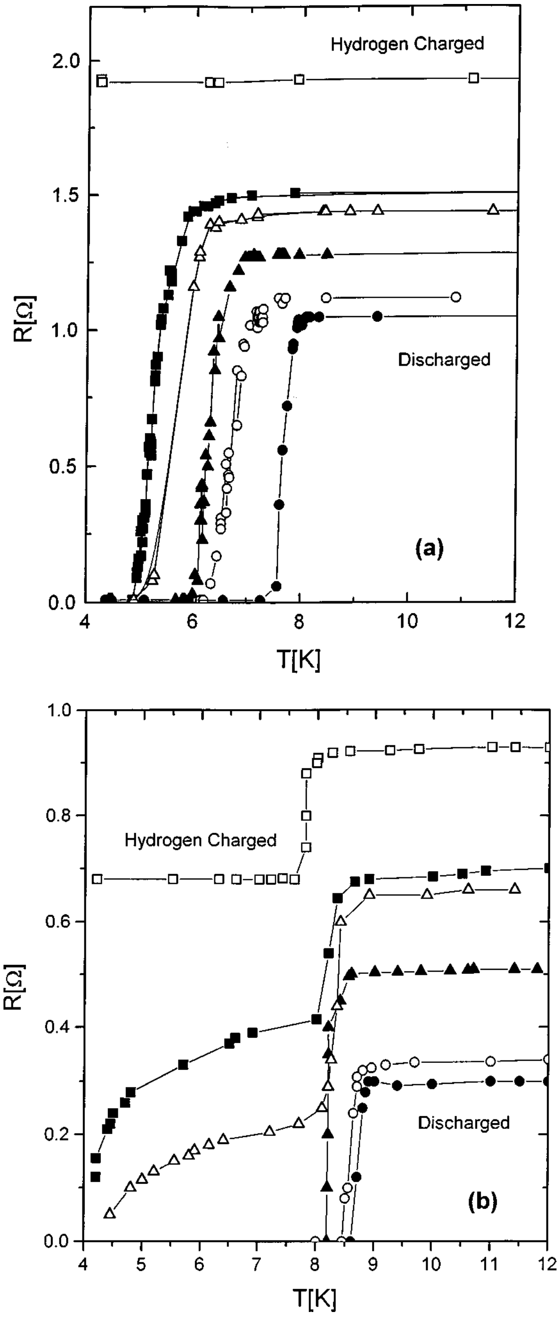

FIG. 1. Resistive superconducting transitions for Nb films charged with various hydrogen concentrations. (a) $R(T)$ for a 600 Å Nb/100 Å Pd showing relatively sharp transitions. (b) $R(T)$ for an 800 Å Nb/100 Å Pd film. The difference in behavior is explained in terms of the properties of a mixture of two phases, a high-T_c phase and a low-T_c phase. In curve (a) the residual resistivity (ρ_0) at 9 K for the sample without hydrogen is about 14 $\mu\Omega$ cm which corresponds to a change in resistance of a factor of 2 when the film is cooled. The addition of about 30% hydrogen changes R about 50%, to a ρ_0 of about 21 $\mu\Omega$ cm at T_c 10 K.

drogen. In general for 600-Å films with ρ at room temperature, of about 28 $\mu\Omega$ cm, the change in resistivity due to hydrogen charging of [H]/[Nb]$\sim$0.6, is about 14 $\mu\Omega$ cm. These measurements, described elsewhere,[10] also show a complete change of the phase diagram in thin layers as compared to the bulk, and there is no evidence of a structural transition into the hydride phase. However, there is evidence for the coexistence of a dilute hydrogen phase (α) with a more dense hydrogen phase (α') similar to the α and α' phases in the bulk phase diagram. For a film 200-Å thick where the phase diagram was measured,[10] we found that the pure α phase exists up until about 10% hydrogen and the boundary for the pure α' phase is about 40% H.

The absence of a transition to a hydride phase, which might be expected at low temperatures, is confirmed by measurements of the temperature dependence of the normal-state resistance over the temperature range from about 300 to 4 K. The data indicate no breaks which would be evidence of a phase change. The slope of the $\rho(T)$ curve, or $\rho_{300}-\rho_{9\ \mathrm{K}}$, for three different concentrations of hydrogen shows that there is basically no change with increasing hydrogen content. This is somewhat surprising since the slope is proportional to the strength of the electron-phonon interaction which is related to λ_{tr} as given by the relationship[13]

$$\rho(T)-\rho_0=\left(\frac{m}{n}\right)_{\mathrm{eff}}\left(\frac{2\pi k_B}{e^2\hbar}\right)\lambda_{\mathrm{tr}}T,$$

and the large T_c changes in Fig. 1 imply that λ_{tr} changes, since λ_{tr} is related to λ. However, we note that λ_{tr} is proportional to the density of states at the Fermi level $N(0)$, but $(m/n)_{\mathrm{eff}}=[N(0)\langle v_F^2\rangle/3]^{-1}$ and, hence, the expression for $\rho(T)$ is independent of $N(0)$. Thus, if T_c changes due to changes in $N(0)$, the slope of $\rho(T)$ vs T will not change, even though λ_{tr} does. Of course, there is still an electronic factor through v_F that will provide some changes, but apparently these are small. Furthermore, the two-phase nature of the sample itself may bias the resistivity measurements in a way that makes changes of ρ with T more insensitive to different concentrations of hydrogen.

In Fig. 2 we show x-ray-diffraction results on the same sample whose resistivity data are presented in Fig. 1(a). In this figure, we plot the normalized powder diffraction intensity against the momentum transfer vector q given by

$$q=\frac{4\pi\sin\theta}{\lambda}.$$

The x-ray data show that the d spacing, $d=2\pi/q$, of the Nb(110) planes, oriented perpendicular to the plane of the films, increases from 2.32 to 2.45 Å when the sample is charged with hydrogen, which corresponds to an increase of 5.5%. Under ''full'' charging the change goes as high as 6–8 % of the pure Nb value. Exposing the hydrogen-charged sample to air caused the discharge of the dissolved hydrogen and a reversible change in the d spacing of the Nb(110) planes. Other work we have done[14] shows that O_2 and H react on the Pd surface and the hydrogen is depleted from the bulk as this reaction progresses. The solid line marked ''α phase'' is provided as a guide to the eye and indicates the lattice spacing of the uncharged α phase sample. As expected the Pd[111] peak, which is also visible in the scan, shows no change from its ambient position. Under these conditions, in air, we have found that hydrogen comes out of the Pd much more rapidly than Nb because of the much smaller heat of the solution.

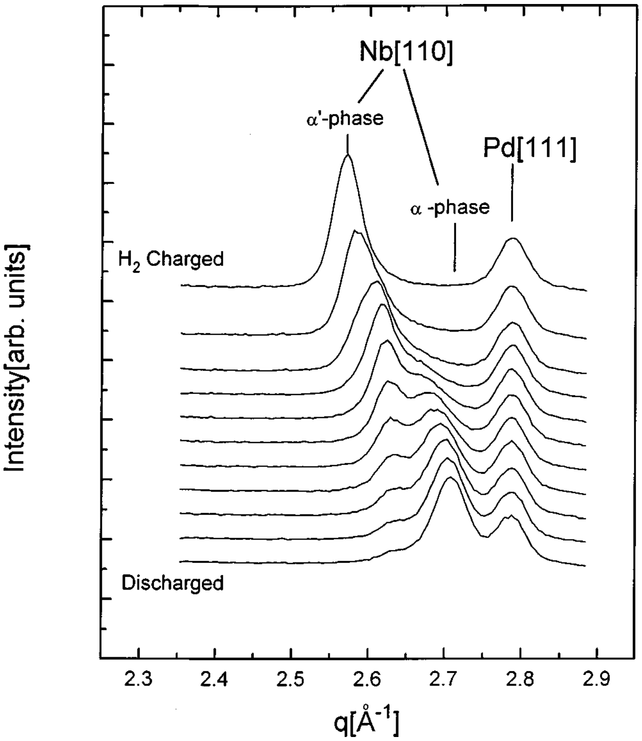

FIG. 2. X-ray powder-diffraction data for a 600 Å Nb/100 Å Pd film that was charged to 10 Torr of hydrogen and allowed to discharge in air. The normalized intensity is plotted against transferred momentum q. The data shows that the Nb[100] peak exhibits large movement from its uncharged position while the Pd[111] peak remains unchanged.

An issue we have only mentioned briefly in the above discussion is the nature of the hydrogen in these thin films. We have made x-ray studies which basically show a lattice gas phase at concentrations below about 10% hydrogen and a correlated α' phase at high concentrations, above about 50%. In between these concentrations the x-ray-scattering results show the coexistence of the two phases. The superconductivity results in Fig. 3 go across this coexistence region and thus the uniform dependence of T_c with concentration of hydrogen must be a result of the coherence length which is larger than the particle size. This point will be discussed below. Furthermore, the uniformity of the transition and the steady decrease with hydrogen composition also imply that this solution phase persists, probably metastably, to low temperatures with no structural changes due to hydride phase formation. The approximate concentration of about H/Nb$\sim$0.3 is estimated from the x-ray results.

A macroscopic picture where it is assumed that the films are composed of a mixture of a high-T_c phase (the low hydrogen density α phase) and a low T_c phase (the high hydrogen density α' phase) can be invoked here to help one understand why some samples show one sharp resistive superconducting transition, while others become superconducting via a double transition like that of Fig. 1(b). In

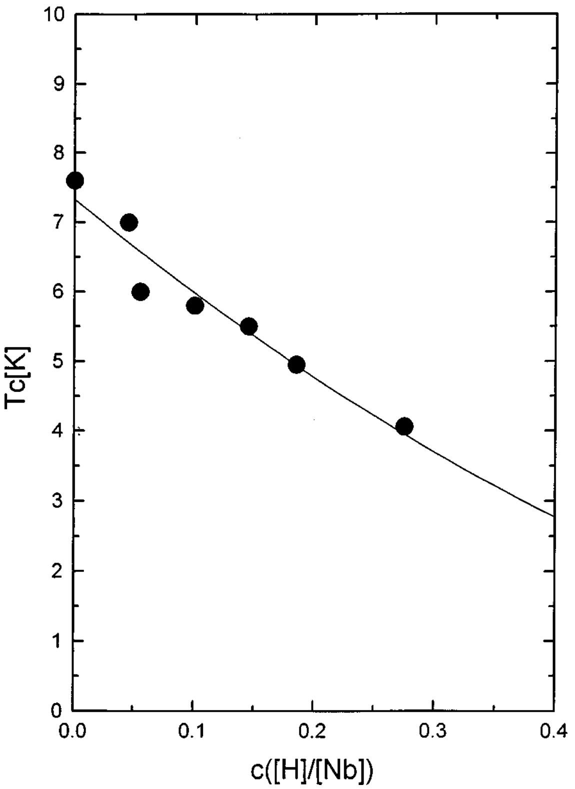

FIG. 3. A fit (solid line) of the measured T_c values (solid circles) versus concentration for the 600 Å Nb/100 Å Pd film. The fit is obtained assuming a two-phase mixture as discussed in the text. Note that for concentrations above 30% hydrogen T_c is depressed below 4 K and we have no measurements of T_c in this regime.

samples of the latter type the film is usually thicker, with larger particle size. In this case the coherence length $\xi_s = \surd(\xi o l)$ in the dirty limit is of the order of 90 Å where $\ell \approx 20$ Å is the mean free path (mfp). Hence ξ_s is smaller than the particle size which for this particular film is of the order of 200 Å. In this case the particles are independently superconducting and although there is some averaging of the order parameter in the α and α' grains, two transitions can be observed. On the other hand, when the particle size is smaller, as in the 600-Å film of Fig. 1(a) ($\xi_s \geqslant$ particle size which is here of the order of 100 Å), the T_c of the separate grains is averaged out. For example, in the Cooper limit[11] the proximity effect on the strength of the interaction for the mixture is simply the volume average for the two phases:

$$[N(o)V]_{\text{eff}} = \frac{f_\alpha [N(o)V]_a + f_{\alpha'} [N(o)V]_{a'}}{f_\alpha + f_{\alpha'}},$$

where f_α and $f_{\alpha'}$ are the volume fractions of the high-T_c and the low-T_c phases as determined by x-ray diffraction. Using the measured value of T_c for the uncharged film which is ≈ 8 K, one calculates an interaction strength $[N(o)V]_\alpha$ of about 0.28. In Fig. 3 we show a plot of the superconducting transition temperature measured for the 600-Å film versus hydrogen concentration as obtained from the lattice expansions determined by x-ray diffraction. On the same graph, we plot the values for T_c calculated using the values of the effective interaction averaged for the two phases in BCS formula for T_c:

$$T_c = \Theta_D \exp\left[\frac{-1}{[N(o)V]_{\text{eff}}}\right].$$

It is found that a value of the effective interaction for the low-T_c phase of about 0.22 produces a reasonable fit for the data. This corresponds to a superconducting transition temperature of about 3 K for this phase at H/Nb$\sim$0.3. Note that the expression for $[N(0)V]_{\text{eff}}$ above, is the simple Cooper formulation; the de Gennes version has somewhat different weighting factors.

IV. THE DEPRESSION OF T_c DUE TO DISORDER

The general depression of the T_c of ultrathin metal films has been investigated in some detail previously for nontransition-metal films such as Pb and Bi. It is generally found that at high enough amounts of disorder, the T_c of the metal is depressed.[15–18] This effect is thought to be due to the localization of electrons and the breakdown of screening in the two-dimensional metal. Ultimately this leads to an activated conduction process and the rapid destruction of superconductivity. In this regime, the mfp is on the order of an interatomic spacing and for a film about one monolayer thick, $R_\square$ is on the order of about 6000 Ω; this is of the order of the value given by the scaling theory of Anderson localization[19] of $\hbar/e^2$. In three dimensions there is a critical resistivity on the order $L\hbar/e^2$, where L is on the order of the interatomic spacing. It should be emphasized here that none of the results presented in this present work are influenced by this limit. The resistivities in these films near 10 K are on the order of 25 $\mu\Omega$ cm, whereas the above limit $\sim$150 $\mu\Omega$ cm.

We mention that mfp's of the order of an interatomic spacing do not necessarily destroy superconductivity in thicker films. In fact, there are amorphous phases of Bi that have a T_c near 6 K,[14] whereas crystalline Bi is a semimetal that is nonsuperconducting. Furthermore, quench condensed films of transition metals such as Mo and W have T_c's that are far above the bulk value.[1] This fact, together with the depression in T_c of disordered Nb, led to the original conjecture that the variation of T_c in disordered transition metals had something to do with smearing of the d-band density of states.[1] It was later argued that this could be characterized by the residual resistivity ρ_0.[3] This argument was especially appealing for the $A15$ superconductors,[20,21] where the structure in the density of states is sharp. However, if one makes a simple estimate from $\Delta E \Delta t = \hbar$,[1,3] one might expect a smearing on the order of 0.5 eV for a mfp of about 5 Å or about an interatomic spacing and a Fermi velocity of 6×10^7 cm/s.[22] Smearing on this order in cryogenically deposited transition metals can possibly account for at least some of the observed changes in T_c (Ref. 1) mentioned above, and this is discussed below.

V. ELECTRONIC CHANGES FOR H IN Nb

To investigate the problem of H in Nb in more detail, in Fig. 4, the density of states (DOS) calculated using the full-potential linearized augmented Slater-type orbital method[23]

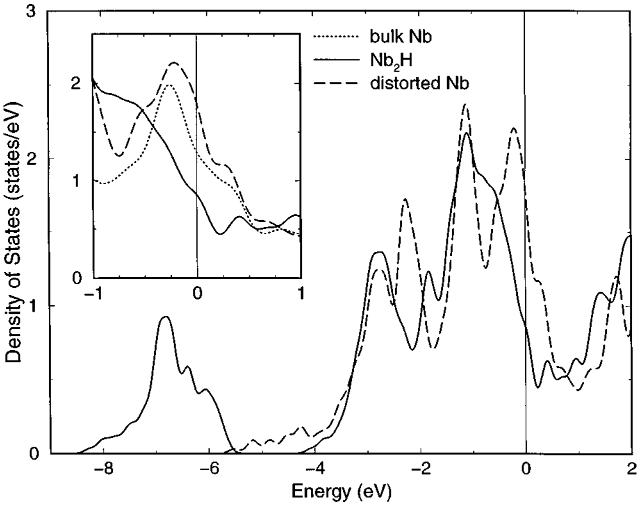

FIG. 4. Calculated density of states for distorted Nb, and Nb_2H, with energies given relative to the Fermi level. The inset gives an expanded view of the density of states near the Fermi level and the DOS for bulk Nb are also shown.

are shown for bulk Nb expanded perpendicular to the plane of the film, and corresponding to the x-ray diffraction determined lattice parameter data at 50% H, and for similarly distorted Nb with an ordered array of H on the usually tetrahedral sites. Other calculations similar to those above show that a homogeneous lattice expansion of up to 10% has almost no effect on $N(0)$: while overall the DOS narrows and increases in magnitude with a lattice expansion, the position of the Fermi level on the downward slope of the DOS is such that $N(0)$ remains almost constant. On the other hand, the effect of an expansion perpendicular to the plane of the film, with the appropriate lattice parameter changes, changes the DOS in such a way that $N(0)$ increases (cf. inset to Fig. 4), which naively would imply an increased T_c in Nb which is contrary to experiment.

The inclusion of H into the Nb lattice expanded perpendicular to the plane of the film causes significant changes in the DOS (cf. Fig. 4), including the formation of a split-off peak below the Nb *d* band. Even though the DOS near the bottom of the *d* bands are severely distorted, the density of states near the Fermi level is well described by a rigid-band picture, as can be seen by comparing the DOS shown in the inset of Fig. 4; a shift of ~0.4 eV aligns the density of states near the Fermi level. Increasing the Fermi energy (E_F) decreases $N(0)$ as it moves E_F down the peak. Because of the rigid-band-like behavior around the Fermi level, we expect this conclusion to hold independent of (reasonable) changes in the concentration of H atoms themselves. Hence, this provides a mechanism for the reduction of T_c. In a similar way, if H were absorbed in Mo or W, T_c might be increased. However, the solubility is too small to try this experiment. It is, of course, clear that this is meant to be a plausibility argument for H concentrations that are similar to those in the experiment. No attempt is made to include the proximity effect in this estimate, or the two-phase nature of the sample.

VI. DISCUSSION

It seems clear that hydrogen changes the density of states by increasing the electron occupancy of the Nb *d* band, and thus provides a mechanism for the decrease of the superconducting transition temperature. As already mentioned, it is also true that disorder is a component in the depression of T_c. For example, in the case of radiation-damaged films[3] an increase of residual resistance at 10 K near 17 $\mu\Omega$ cm, which is comparable to the residual ρ_0 of the ''as-sputtered film,'' causes a reduction of T_c on the order of a 4 K. This is a rate of depression of about 0.22 K/$\mu\Omega$ cm. In a similar manner, adding oxygen to bulk Nb depresses T_c at a rate of about 0.2 K/$\mu\Omega$ cm.[24] This depression of T_c with disorder has already been discussed[3,4,21] and Testardi and Matthiess[21] give a calculated value of about 0.2 K/$\mu\Omega$ cm for Nb due to smearing of the electronic properties. In contrast we emphasize that in these present results the T_c is depressed to about 5 K from 7.8 K for a change in ρ_0 due to the addition of hydrogen of about 7 $\mu\Omega$ cm, or a rate of 0.4 K/$\mu\Omega$ cm. Hence, the hydrogen depresses T_c at twice the rate of disorder alone and we attribute this increase to the lowering of the density of states due to the hydrogen itself in addition to the smearing due to disorder. Of course, the situation is somewhat more complex because of the two-phase nature of the material when hydrogen is added. However, the intuitive volume averaging of the interaction makes physical sense.

It is interesting that in the multilayer system[7] T_c decreases about 4.5 K with a change in ρ of about 70 $\mu\Omega$ cm or less than 0.1 K/$\mu\Omega$ cm. In this case the effect of disorder as hydrogen is added is much more severe and can amount to 2 $\mu\Omega$ cm/at. % H, which is higher than in our films where the change is about 0.6 $\mu\Omega$ cm/at. % H (similar to the bulk value). Some of this large change in the multilayers might be some interfacial effect which is very sensitive to the defects caused by the addition of hydrogen. If this is true, the interfacial component of the disorder might not directly affect T_c.

VII. SUMMARY

The depression of T_c in Nb layers has been studied for H concentration up to about 30 at. %. In these thin films the hydride is apparently not formed, although at concentrations above a few percent there is a mixture of a dilute and more concentrated hydrogen phases. The depression of T_c is significantly greater than that due to disorder alone, and this is attributed to changes in the density of states near E_f due to changes in the Nb *d* band caused by the addition of hydrogen. A simple proximity effect model is used to account for the two-phase nature of the material when hydrogen is added.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Division of Materials Science, under Contract No. DE-AC02-98CH10886. X-ray spectroscopy was done at the National Synchrotron Light Source (NSLS) which is also supported by the U.S. Department of Energy, Division of Materials Science.

[*] Permanent address: Department of Physics, Birzeit University, West Bank.

[†] Permanent address: Sandia National Laboratory, Albuquerque, New Mexico.

[1] J. E. Crow, M. Strongin, R. S. Thompson, and O. F. Kammerer, Phys. Lett. **30A**, 161 (1963).

[2] M. M. Collver and R. H. Hammond, Phys. Rev. Lett. **30**, 92 (1973).

[3] H. L. Lutz, H. Wiesmann, M. Gurvitch, A. Goland, O. F. Kammerer, and M. Strongin, *Superconductivity in d and f Band Metals*, edited by P. H. Douglass (Plenum, New York, 1976), p. 535.

[4] C. M. Varma and R. C. Dynes, *Superconductivity in d and f Band Metals* (Ref. 3), p. 507.

[5] S. Moehlecke and Z. Ovadyahu, Phys. Rev. B **29**, 6203 (1984).

[6] W. DeSorbo, Phys. Rev. **132**, 107 (1963). See, also, B. Stritzker and H. Wuhl, *Superconductivity in Metal Hydrogen Systems*, Topics in Applied Physics Vol. 29, edited by G. Alefeld and J. Volkl (Springer-Verlag, Berlin, 1978), p. 243.

[7] C. Uher, J. L. Cohn, P. F. Micelli, and H. Zabel, Phys. Rev. B **36**, 815 (1987).

[8] M. A. Pick, J. W. Davenport, M. Strongin, and G. J. Dienes, Phys. Rev. Lett. **43**, 286 (1979).

[9] S. Moehlecke, C. F. Majrzak, and M. Strongin, Phys. Rev. B **31**, 6804 (1985).

[10] G. Reisfeld, N. Jisrawi, M. W. Ruckman, and M. Strongin, Phys. Rev. B **53**, 4974 (1996).

[11] P. G. de Gennes, Rev. Mod. Phys. **36**, 225 (1964); L. Cooper, Phys. Rev. Lett. **6**, 698 (1961).

[12] H. Pfeiffer and H. Peisl, Phys. Lett. **60A**, 363 (1977).

[13] P. B. Allen, Phys. Rev. B **3**, 905 (1975).

[14] G. Reisfeld and M. Strongin, Chem. Phys. Lett. **246**, 85 (1995).

[15] M. Strongin, R. S. Thompson, O. F. Kammerer, and J. E. Crow, Phys. Rev. B **1**, 1078 (1970).

[16] R. C. Dynes, A. E. White, J. M. Graybeal, and J. P. Garno, Phys. Rev. Lett. **57**, 2195 (1986).

[17] D. B. Havland, Y. Liu, and A. M. Goldman, Phys. Rev. Lett. **62**, 2180 (1989).

[18] J. M. Graybeal and M. R. Beasley, Phys. Rev. **20**, 4167 (1984).

[19] Y. Imry and M. Strongin, Phys. Rev. B **24**, 6353 (1981).

[20] H. Wiesmann, M. Gurvitch, A. K. Ghosh, H. Lutz, O. F. Kammerer, and M. Strongin, Phys. Rev. B **17**, 122 (1978).

[21] L. R. Testardi and L. F. Mattheiss, Phys. Rev. Lett. **41**, 1612 (1978).

[22] M. Gurvitch, Phys. Rev. B **34**, 540 (1986).

[23] G. Fernando, J. W. Davenport, R. E. Watson, and M. Weinert, Phys. Rev. B **40**, 2757 (1989).

[24] C. C. Koch, J. O. Scarbrough, and D. M. Kroeger, Phys. Rev. B **9**, 888 (1974).