Anomalous heat capacities of niobium and tantalum below 1 K†

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The specific heat of superconducting Nb has been measured in the temperature range 0.06–2 K in an outgassed condition (initial H and D concentrations $\lesssim 1$ ppm atomic) and with H or D added as interstitial solutes. The specific heat of superconducting and normal Ta has also been measured in the outgassed condition and with H intentionally added. The addition of H or D to these bcc transition metals produces an isotope-dependent specific-heat anomaly which appears to be related to a displacive motion of the interstitial H or D. No evidence is found in either metal which would be suggestive of a second superconducting energy gap.

I. INTRODUCTION

We report here the results of a project which began as an investigation of the superconducting properties of the bcc transition metals V, Nb, and Ta, and ended as a study of the thermal behavior of dissolved hydrogen in these metals.[1]

The electronic properties of the transition metals are often described in terms of two electronic conduction bands. It has been suggested that if the scattering of electrons between these two bands is sufficiently weak, each of the two bands may undergo a separate transition into the superconducting state.[2] That is, two energy gaps may appear in the conduction bands. Anomalies have been observed in the measured properties of the superconducting metals V, Nb, and Ta. These were quite naturally interpreted from the viewpoint of the two-gap theory. Included were the specific heat,[3–10] electron tunneling,[11–14] acoustic attenuation,[15,16] magnetic effects,[17–20] surface impedance,[21] thermal conductivity,[22–24] the associated effects of impurities,[25–27] and the associated effects of alloying.[10,28] In brief, the anomalies were interpreted to arise not from variations due to anisotropy in the Fermi surface, but rather from the appearance of an additional energy gap. For the case of Nb it was deduced from some measurements that the ratio of the energy gap in the conduction band associated with the dominant *d* electrons to that associated with the *s* electrons was ≈ 10.

A thermal-conductivity measurement on Nb carried out in our laboratory was interpreted as not giving evidence for a second, small gap,[29] although this interpretation was later questioned.[30] We therefore proceeded to measure the heat capacity of this transition-metal superconductor, and showed that an anomaly previously associated with the second gap was more likely associated with residual H impurities.[31] In addition, no evidence for a second superconducting energy gap has been observed in the more recent measurements of acoustic attenuation[32] or electron tunneling.[33] We therefore adopt the view in the present paper that the appropriateness of the two-gap model to the transition-metal superconductors has yet to be demonstrated, and will proceed to a discussion primarily of the low-temperature behavior of interstitial H and D.

The results of the heat-capacity measurements are presented in Secs. II and III. The calorimetric technique has been discussed in detail elsewhere.[34] The over-all accuracy is better than 2% as verified by measurements on high-purity annealed Cu. All data are relative to the ^{3}He vapor-pressure scale extrapolated to lower temperatures using magnetic thermometry.[35] Because of the large number of different measurements, a brief discussion will accompany each presentation of data.

II. Nb: RESULTS AND DISCUSSION

Some of the data on Nb (Ref. 36) are presented in Figs. 1–3; other data will be discussed in the text. Identical symbols are used to identify the same sample on each figure, and a letter is also assigned to each sample to provide ready identification in the text. In Fig. 1 the data are presented in the conventional manner for metals. The dashed line represents the lattice or phonon contribution to the specific heat based on acoustic and other *noncalorimetric* determinations of the low-temperature limit of the Debye temperature.[37] Also included is a very slight contribution due to conduction electrons above ≈ 1 K. In Fig. 2 the lattice and electronic contributions have been subtracted to give the "anomalous" specific heat C_A. Figure 3 provides a plot of C_A divided by temperature T so that the entropy associated with the anomaly

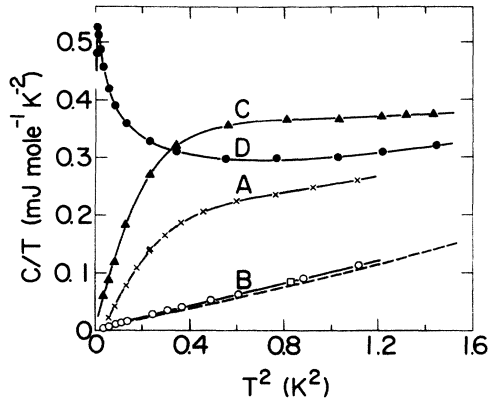

FIG. 1. Specific heat of Nb divided by temperature T, vs T^2. The dashed line is the calculated contribution from phonons and electrons. The symbols and letters are the same for Figs. 1–3. A, as received sample; B, two vacuum-annealed samples (most squares lie exactly under the circles); C, hydrogen interstitial solutes added; D, deuterium interstitial solutes added.

may be estimated.

The specific heat of Nb in the as-received condition, curve A, exhibited an anomaly similar in magnitude and shape to that observed in other laboratories.[3,7,10] Annealing at 2250 °C in a vacuum of $\approx 3\times10^{-6}$ Torr for ≈ 2 h produced curve B, the data from two different samples being identical in magnitude. The magnitude of the anomaly has been greatly reduced.[38] Severe cold working of an as-received sample produced a result similar to curve B. These results suggested that the anomaly might be associated with the presence of H. The H would be effectively removed from solution in the metal either by outgassing during the high-vacuum anneal, which would produce an initial hydrogen concentration of $\lesssim 1$ ppm atomic, or by precipitation and trapping at dislocations produced by cold working.[39,40]

To test this possibility, hydrogen and deuterium were diffused separately into two samples using H_2 or D_2 gas which was purified by diffusion through a Pd membrane. (The concentration of H_2 in the D_2 gas was $\lesssim 1\%$.) To accomplish this doping, each sample was heated in the H_2 or D_2 gas to a maximum temperature of 700 °C, and the gas pressure was regulated to obtain the desired H or D concentration. (At 700 °C, the content of other interstitial gases would not be significantly changed.) The sample was cooled while varying the pressure to maintain that concentration of H or D.[41] The surfaces of the samples were then oxidized at about 100 °C to retain a constant hydrogen or deuterium concentration. Introduction of about 3000-ppm (atomic) H or D resulted in curves C and D (Figs. 1–3), respectively. As a check the hydrogen was removed from one sample (corresponding to curve C) and replaced with deuterium. Curve E of Fig. 2 resulted, showing that the isotope effect is real and reproducible.

As may be seen in Figs. 1 and 2, even the annealed and outgassed samples indicate a small anomaly. We do not believe this is related to normal electrons associated with a second energy gap since the temperature dependence is very close to that of the anomaly clearly associated with H impurity. Rather we believe it is caused by a small residual H impurity, since a H content of < 1 ppm atomic would account for the anomaly and it is very

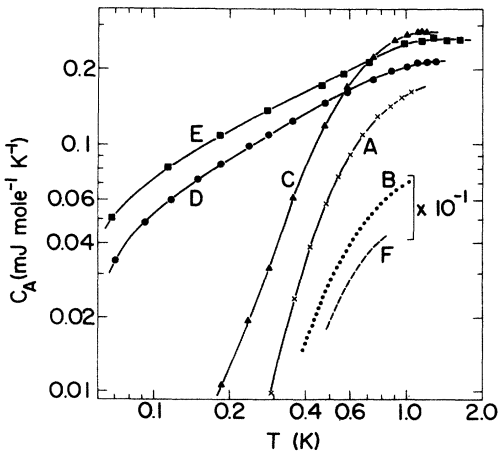

FIG. 2. Specific heat of Nb after the lattice and electronic contributions have been subtracted. Curve E, deuterium interstitial solutes added, see text for details; F, vacuum annealed and deformed. Note that curves B and F are more than a factor of 10 smaller in magnitude than the other curves.

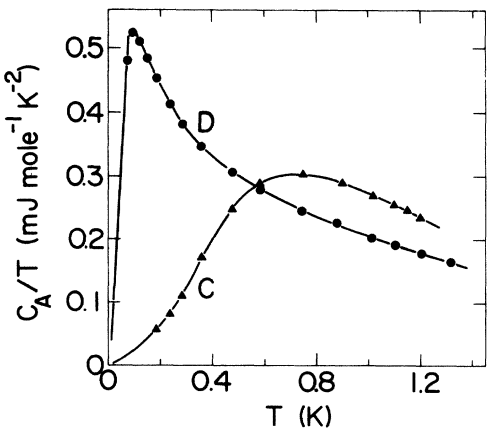

FIG. 3. Specific heat of hydrogen- (C) or deuterium- (D) doped samples of Nb with the lattice and electronic contributions subtracted, divided by temperature. The area under the curves gives the entropy associated with the H or D impurities.

difficult to remove all traces of H from Nb.[42] Bending one of the annealed and outgassed samples produced curve F of Fig. 2. The strain caused a reduction in magnitude of the anomaly just as cold working was observed to reduce the anomaly clearly associated with the H impurity. The reduction in magnitude of the heat capacity with strain also indicates that the anomaly is not to be associated with eigenstates of dislocations.[43]

We observed that the condensation of gases or water vapor onto the samples during cryostat cooldown did not change the measured heat capacity by more than the experimental precision of 0.2%, nor did abrasion of the surfaces of the annealed and outgassed samples with 27-μm airborne abrasive. However, when sample E was raised to a temperature of ≈ 50 K for a period of 30 h, there was a small systematic reduction in C_A by 2.3 (± 0.4)% below 0.6 K. This last effect may be associated with additional precipitation of the deuteride since the alloys are supersaturated at 50 K[44] and the deuterium is still highly mobile at 50 K.[45]

On the basis of the above results, we concluded that there is no evidence in the heat-capacity data to support the suggestion of a second superconducting energy gap in Nb. An important test of the two-gap interpretation of the heat-capacity anomaly is whether the anomaly is absent in the normal state produced by application of a field greater than H_{c2}. Although our cryostat is not equipped with an appropriate magnet, the paper by Shen *et al.*[3] did present data for the normal state. They measured two samples which showed different specific-heat anomalies in the superconducting state. However, a difference in specific heat of about the same magnitude is also apparent in their normal-state data.[46] This result and the large isotope effect observed in the present paper (Figs. 1–3) suggest that the anomaly is not electronic in origin, but is associated with the lattice. Hence the anomaly is probably caused by motion of the H or D in the Nb lattice.

During cooling most of the H (or D) precipitates as the β-phase hydride.[44] It is suspected, however, that the anomaly is associated with H in the α phase rather than the β phase. As evidence for this we note that the magnitude of the anomaly changes by only a factor of ≈ 2 for a factor of 100 variation in H content.[47] This is in accord with the phase diagram and the high H diffusivity in Nb.[48] The quantity of H remaining in solution in the α phase at low temperature depends primarily on the rate at which the sample is cooled.[42] This is also consistent with the observed reduction in C_A for sample E when this sample was held at 50 K for many hours as mentioned above. The cryostat and sample could not, however, be cooled very rapidly, which would have provided a definitive test of this suggestion.

Earlier in this paper we argued that the specific-heat anomaly is associated with the lattice. The observation of a large isotope effect suggests the possibility that the H or D is undergoing a tunneling motion in the Nb lattice. If such tunneling occurs, it should provide a probe of the local lattice potential. Another probe of the lattice potential is provided by measurements of diffusion. The H diffusivity in Nb deviates from a classical (Arrhenius) temperature dependence at low temperature,[49] and exhibits a nonclassical isotope effect.[45] Recent theoretical treatments attribute these effects to quantum tunneling of the interstitial.[50]

If one assumes that the observed specific-heat anomaly does arise from a tunneling motion,[51] the atomic fraction of impurity associated with C_A may be deduced from the entropy obtained from Fig. 3. Assuming the curves C and D extrapolate linearly to $C_A/T = 0$, one concludes that the H or D responsible for C_A is roughly 50 ppm atomic. This is a small fraction of the 3000 ppm introduced into these samples and is consistent with most of the hydrogen being located in the precipitated hydride or deuteride.

In summary, the data obtained thus far on Nb are consistent with the heat-capacity anomaly being caused by a localized mode of the lattice associated with a H or D interstitial in the α phase. The large isotope effect suggests that the localized

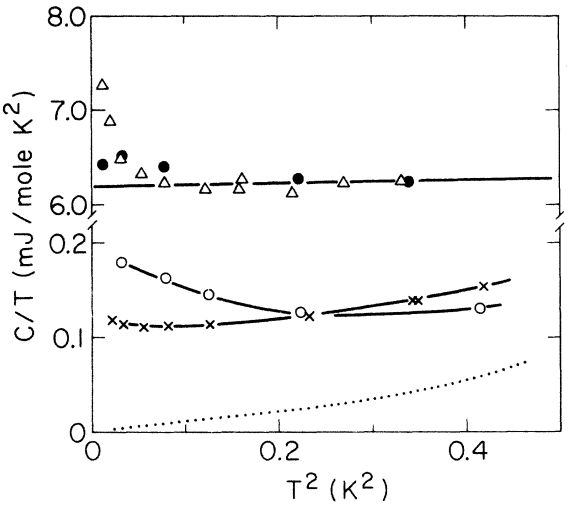

FIG. 4. Specific heat of Ta, divided by temperature T, vs T^2. The upper data are for the normal state, the lower data are for the superconducting state. Note the $\times 10$ change in vertical scale between the two sets of data. The dotted line is the calculated contribution from lattice phonons and electrons. ●, vacuum annealed normal state; △, vacuum annealed and H doped, normal state; ○, vacuum annealed superconducting state; ×, fast relaxation portion of the specific heat in the vacuum-annealed and H-doped samples (qualitative only, see text).

mode may result from tunneling. Our data show no evidence for a second superconducting energy gap.

III. Ta: RESULTS AND DISCUSSION

The specific-heat data for a Ta sample[52] annealed at 2100 °C in a vacuum of 7×10^{-6} Torr for ≈3 h are shown in Fig. 4 for both the superconducting and normal states, the latter having been obtained in a magnetic field of 3800 G. For the normal state we obtain $\gamma = (6.2\pm0.2)$ mJ/mole K^2 for the electronic specific-heat coefficient, which may be compared with Gschneidner's[53] composite value of (5.84 ± 0.3) mJ/mole K^2. The superconducting state for the out-gassed specimen exhibits a heat capacity in excess of that expected from the lattice.[54] This additional specific heat C_A is shown on Fig. 5. It is unlikely that this C_A is associated with normal electrons related to a second superconducting energy gap. The temperature dependence is neither suggestive of normal-state electrons nor of a superconducting transition in a well-annealed sample. In addition, the thermal-transport measurements of the following paper[55] give no indication of the presence of such normal-state electrons. We suggest that this additional heat capacity arises from impurities within the sample and would correspond to ≈10 ppm (atomic) of some, possibly magnetic, impurity.[52] This additional heat capacity seems not to have been present in the measurements of Ref. 10.

A second sample of the same starting material was also vacuum annealed. Then H was diffused in to a concentration of ≈1% (atomic)[41] using the same methods as for the Nb samples. Two distinct features were evident in the heat-capacity measurements on this H-doped sample. First, there was a large additional contribution to the specific heat at low temperatures in both the superconducting and normal states and, second, whatever caused the additional heat capacity was thermally linked to the lattice very weakly in both the normal and superconducting states. In other words application of a heat pulse to the sample caused the lattice (and thermometer) to warm immediately. Then slowly, with a time constant of ≈1 sec at 0.3 K, the thermal energy leaked into the additional heat capacity causing the lattice and thermometer to cool. This experimental problem involving weakly coupled energy levels has been encountered previously in measurements of the nuclear-quadrupole heat capacity of superconducting metals.[56]

The relatively long internal relaxation time in the H-doped sample was not unexpected. We had attempted to observe a finite thermal relaxation effect in Nb, but were unsuccessful since the time constant was too short. The presence of this effect

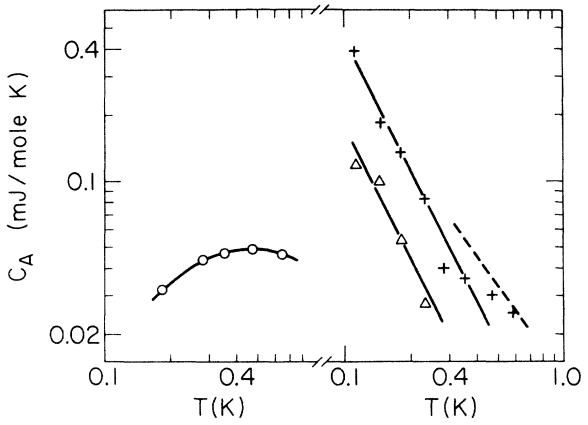

FIG. 5. Left: the portion of the specific heat of the annealed undoped Ta sample which is not attributed to lattice phonons and electrons. Right: *additional* specific heat resulting from the introduction of H into annealed Ta. Δ, qualitative normal-state data; +, qualitative superconducting-state data. The dashed line is the specific-heat anomaly observed in superconducting Ta in Ref. 10.

in Ta prevented us from making quantitative specific-heat measurements on the H-doped sample. We could however, obtain qualitative measurements of the specific heat related to the rapid internal relaxation, namely, the lattice contribution and anything thermally coupled tightly to the lattice. This is shown by the symbol × in Fig. 4 for the superconducting state. These qualitative data are very similar to the quantitative data of the undoped superconducting sample.

A qualitative measure can also be obtained of the specific heat related to the slow internal relaxation time, which appeared with the addition of H to the lattice. This additional specific heat is shown in Fig. 5 for both the normal state and the superconducting state. The two sets of data differ by a factor of ≈2, which may reflect our ability to extract the information from the raw data. The total specific heat of the doped sample in the normal state is shown on Fig. 4. Since quantitative measurements could not be obtained on the additional heat capacity of doped samples at very low temperatures, no attempt was made to diffuse D into Ta.

The straight lines through the specific-heat data associated with the addition of H, Fig. 5, have been drawn with a slope of −2. This temperature dependence would be consistent with a Schottky anomaly, the peak of which is located near or below 0.1 K. Also shown by the dashed line on Fig. 5 is that fraction of the specific heat of Ref. 10 which is not associated with lattice phonons or *d*-state electrons. The results of Fig. 5 suggest that the specific-heat anomaly in nominally pure Ta dis-

cussed in Ref. 10 may also be caused by interstitial H, which is difficult to avoid in Ta.[57]

Clearly the present work indicates a heat-capacity anomaly associated with the addition of H in Ta, but the mechanism producing the anomaly is not so clear. A few possibilities are discussed next. The anomaly could be related to a nuclear-quadrupole interaction with a noncubic lattice field caused by interstitial H. However, this seems unlikely since the long internal relaxation time persists in the normal state. In addition, alloying with Nb was found to decrease the magnitude of the anomaly in Ref. 10, whereas if quadrupole interactions were responsible for the anomaly the magnitude would not be expected to decrease. For similar reasons the additional heat capacity probably is not associated with a hyperfine interaction in the β-phase precipitate.

As discussed in the following paper,[55] locally high densities of dislocations were produced in the H- and D-doped samples at the β-phase precipitates formed during cooling. Eigenstates associated with the dislocations would contribute to the specific heat.[43] However, the resonant frequency of dislocations in Ta is too high to explain the heat-capacity anomaly,[58] and in addition the dislocation density[55] was not sufficiently large. The specific-heat anomaly could be associated with diffusive motion or vibration of interstitial H as appears to be the case in Nb. If this were true, the Schottky character of the anomaly would suggest a tunneling mode.

IV. CONCLUSIONS

Specific-heat measurements on the group-V*B* transition metals V,[1] Nb, and Ta demonstrate a low-temperature contribution to the heat capacity associated with the introduction of interstitial H or D. A tunneling motion of the H or D in the α phase of the bcc lattice would be consistent with the information and data presently at hand, including the measurements on thermal transport in Nb.[55] No evidence was obtained which would be strongly suggestive of a second superconducting energy gap in these metals.

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[1]The work on vanadium has been presented separately by G. J. Sellers, M. Paalanen, and A. C. Anderson [Phys. Rev. B (to be published)].

[2]H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Lett. 3, 552 (1959).

[3]L. Y. L. Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Lett. 14, 1025 (1965). The magnetic-field value given as 2.5 kOe in Fig. 1 of this paper is apparently in error, as this is well below H_{c2}. See J. Ferreira da Silva, E. A. Burgemeister, and Z. Dokoupil [Physica 41, 409 (1969)]. The onset of the heat-capacity anomaly was also observed by H. A. Leupold and H. A. Boorse [Phys. Rev. 134, A1322 (1964)], and by B. J. C. van der Hoeven, Jr. and P. H. Keesom [Phys. Rev. 134, A1320 (1964)].

[4]C. C. Sung and L. Y. L. Shen, Phys. Lett. 19, 101 (1965).

[5]T. Soda and Y. Wada, Prog. Theor. Phys. 36, 1111 (1966).

[6]B. T. Geilikman, R. O. Zaitsev, and V. Z. Kresin, Fiz. Tverd. Tela 9, 821 (1967) [Sov. Phys.-Solid State 9, 642 (1967)].

[7]A. A. Melo and S. T. Spence, in *Proceedings of the Twelfth International Conference on Low Temperature Physics*, edited by E. Kanda (Academic of Japan, Tokyo, 1971), p. 281.

[8]R. H. Burkel and W. S. Chow, Phys. Rev. B 3, 779 (1971).

[9]I. I. Fal'ko and V. L. Fal'ko, Solid State Commun. 10, 409 (1972).

[10]T. Satoh, A. Sawada, and M. Yamamoto, in *Proceedings of the International Conference on Low Temperature Physics and Chemistry*, *LT*13 (Plenum, New York, to be published). The observed decrease in the specific-heat anomaly in Nb-Ta alloys might be related to the low-temperature trapping of H at the substitutional impurity sites.

[11]V. Radhakrishnan, Phys. Status Solidi 18, 113 (1966).

[12]J. W. Hafstrom and M. L. A. MacVicar, Phys. Rev. B 2, 4511 (1970).

[13]M. L. A. MacVicar, Phys. Rev. B 2, 97 (1970).

[14]L. Y. L. Shen, Phys. Rev. Lett. 24, 1104 (1970).

[15]I. M. Tang, Phys. Rev. B 2, 2581 (1970); B 3, 3960 (1971).

[16]L. L. Lacy and A. C. Daniel, Phys. Rev. Lett. 27, 1128 (1971).

[17]V. Radhakrishnan, Nuovo Cimento 48, 111 (1967); Phys. Status Solidi 20, 783 (1967).

[18]V. K. Wong and C. C. Sung, Phys. Rev. Lett. 19, 1236 (1967).

[19]C. C. Sung, Phys. Rev. 187, 548 (1969).

[20]I. M. Tang, Phys. Lett. 32A, 185 (1970); Phys. Rev. B 2, 3582 (1970); Phys. Status Solidi 56, K47 (1973).

[21]I. M. Tang, Phys. Rev. B 2, 4504 (1970).

[22]R. Vasudevan and C. C. Sung, Phys. Rev. 144, 237 (1966).

[23]J. R. Carlson and C. B. Satterthwaite, Phys. Rev. Lett. 24, 461 (1970).

[24]I. M. Tang, Phys. Lett. 31A, 480 (1970).

[25]C. C. Sung and V. K. Wong, J. Phys. Chem. Solids 28, 1933 (1967).

[26]W. S. Chow, Phys. Rev. 172, 467 (1968).

[27]I. M. Tang, Phys. Rev. B 2, 129 (1970); Phys. Rev. B 2, 1299 (1970).

[28]B. Ya. Sukharevskii, I. S. Shchetkin, and I. I. Fal'ko Zh. Eksp. Teor. Fiz. 60, 277 (1971) Sov. Phys.-JETP 33, 152 (1971)].

[29]A. C. Anderson, C. B. Satterthwaite, and S. C. Smith, Phys. Rev. B 3, 3762 (1971). See also A. C. Anderson and S. C. Smith, J. Phys. Chem. Solids 34, 111

(1973).
[30]P. Kumar and S. N. Gupta, Phys. Rev. B 6, 2642 (1972).
[31]G. J. Sellers, A. C. Anderson, and H. K. Birnbaum, Phys. Lett. 44A, 173 (1973).
[32]D. P. Almond, M. J. Lea, and E. R. Dobbs, Phys. Rev. Lett. 29, 764 (1972). See also E. M. Forgan and C. E. Gough, J. Phys. F 3, 1596 (1973).
[33]M. H. Frommer, J. Bostock, Kofi Agyeman, R. M. Rose, and M. L. A. MacVicar, Solid State Commun. 13, 1357 (1973).
[34]G. J. Sellers and A. C. Anderson, Rev. Sci. Instrum. (to be published).
[35]A. C. Anderson, R. E. Peterson, and J. E. Robichaux, Rev. Sci. Instrum. 41, 528 (1970).
[36]Origin of the polycrystalline Nb material is uncertain, approximate impurity content (ppm atomic): W, 3; Ta, 50; Mo, 2; Zr, 6; Cu, 50; Ni, 4; Fe, 4; Mn, 4; Cr, 4; K, 10; Si, 20; Al, 10. The samples were spark cut from the same plate. Masses for the four samples varied from 10 to 65 g.
[37]G. A. Alers and D. L. Waldorf, Phys. Rev. Lett. 6, 677 (1961); R. Weber, Phys. Rev. 133, A1487 (1964); K. J. Carroll, J. Appl. Phys. 36, 3689 (1965); R. I. Sharp, J. Phys. C 2, 421 (1969). A value of Θ_D deduced from these sources is adjusted to $\Theta_D = 274 \pm 3$ K appropriate to the T_{62} temperature scale used in the present work. See J. C. Holste, Phys. Rev. B 6, 2495 (1972).
[38]This result has also been observed by C. E. Gough, in Ref. 10.
[39]Y. Sasaki and T. Matsumoto, Jap. J. Appl. Phys. 11, 617 (1972).
[40]C. Baker and H. K. Birnbaum, Scr. Metall. 6, 851 (1972).
[41]B. Siegel and G. G. Libowitz, in *Metal Hydrides*, edited by W. M. Mueller, J. P. Blackledge, and G. G. Libowitz (Academic, New York, 1968), p. 545.
[42]K. Faber and H. Schultz, Scr. Metall. 6, 1065 (1972).
[43]J. Bevk, Philos. Mag. 28, 1379 (1973). Presumably this measurement also includes the contribution to the heat capacity caused by the static-strain fields of dislocations. See Y. Hiki, T. Maruyama, and Y. Kogure, J. Phys. Soc. Jap. 34, 725 (1973).
[44]R. J. Walter and W. T. Chandler, Trans. Metall. Soc. AIME (Am. Inst. Min. Metall. Pet. Eng.) 233, 762 (1965); D. Westlake, *ibid.* 245, 287 (1969).
[45]R. Mattas and H. K. Birnbaum (unpublished).
[46]The similarity in separation of the two sets of curves in Ref. 3 is obscured by a factor of 4 difference in scales.
[47]P. Rödhammer (unpublished). We are grateful to O. Vilches for bringing this work to our attention.
[48]H. K. Birnbaum and C. A. Wert, Ber. Bunsenges. Phys. Chem. 76, 806 (1972), and papers cited therein.
[49]C. Baker and H. K. Birnbaum, Acta Metall. 21, 865 (1973).
[50]C. P. Flynn and A. M. Stoneham, Phys. Rev. B 1, 3966 (1970); J. A. Sussmann and Y. Weissman, Phys. Status Solidi 53, 419 (1972), and papers cited therein.
[51]V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. 42, 201 (1970).
[52]Ta obtained from Wah Chang Corp. Two independent analyses gave W, 100 ppm atomic; Nb, 80; Mo, 40; Fe, ≤ 2; Zr, ≤ 10; Pt, 4; Au, 3; Hf, 2; other metals ≤ 1. The samples were not analyzed for O content. The masses for the two samples were ≈ 42 g.
[53]K. A. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 275.
[54]R. G. Leisure, D. K. Hsu, and B. A. Seiber, J. Appl. Phys. 44, 3394 (1973), and papers cited therein.
[55]S. G. O'Hara, G. J. Sellers, and A. C. Anderson, following paper, Phys. Rev. B 10, 2777 (1974).
[56]N. E. Phillips, CRC Crit. Rev. Solid State Sci. 2, 467 (1971).
[57]R. Handa, T. Suganuma, and H. Kimura, Scr. Metall. 6, 483 (1972).
[58]S. G. O'Hara and A. C. Anderson, Phys. Rev. B 10, 574 (1974).