[13] H. Birecki, R. Schaetzing, F. Rondelez, and J. D. Litster, Phys. Rev. Lett. 36, 1376 (1976).

[14] K.-C. Lim and J. T. Ho, to be published

[15] R. S. Pindak, C.-C. Huang, and J. T. Ho, Phys. Rev. Lett. 32, 43 (1974).

[16] P. G. de Gennes, private communication.

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# Nitrogen-Hydrogen Interstitial Pair in Niobium as a New System Showing Atomic Tunneling

C. Morkel and H. Wipf
*Physik-Department der Technischen Universität München, D-8046 Garching, West Germany*

and

K. Neumaier
*Zentralinstitut für Tieftemperaturforschung der Bayerischen Akademie der Wissenschaften, D-8046 Garching, West Germany*

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We have made low-temperature specific-heat measurements demonstrating tunneling of hydrogen trapped by interstitial nitrogen in niobium.

Tunneling effects of interstitial hydrogen in metals are the subject of continuous theoretical and experimental interest, stimulated mainly by the marked nonclassical behavior observed for hydrogen diffusion.[1] However, the most straightforward experimental evidence so far for hydrogen tunneling in metals is reported by Sellers, Anderson, and Birnbaum,[2] who found that a low-temperature specific-heat anomaly in niobium (previously associated with a second energy gap in superconducting niobium[3]) was related to the presence of hydrogen impurities. The isotope effect observed for this anomaly clearly indicated that it was caused by hydrogen tunneling.

To know the atomistic structure of the hydrogen-tunneling complex causing this specific-heat anomaly in niobium is important for a theoretical understanding of hydrogen tunneling in metals, with all its consequences on hydrogen-diffusion theories[1]; furthermore, it is a prerequisite for any detailed experimental investigation (e.g., in low-temperature neutron-scattering experiments).

So far, this atomistic structure is not know. Two diverging suggestions have been made,[4,5] proposing hydrogen tunneling either among tetrahedral and triangular interstices within a polaronlike distorted lattice region not requiring the presence of other lattice defects,[5] or among trap sites[4] provided by (immobile) nitrogen or oxygen interstitials.[6-9] In this Letter, we report on a systematic experimental study made by low-temperature specific-heat measurements in order to determine the structure of the hydrogen tunneling complex in niobium. In particular, to investigate the influence of impurity trap centers, measurements were made (a) on highly purified niobium, (b) on samples doped with either hydrogen or nitrogen, and (c) on samples doped with both hydrogen and nitrogen. Nitrogen interstitials seem especially appropriate for a study of the influence of traps since their low-temperature trapping behavior is well established.[8,9] Particularly for nitrogen concentrations larger than those of hydrogen (as in the case of our N-doped samples), and for slow cooling rates (typically 1 K/min in our experiments), all hydrogen atoms are trapped at low temperatures under formation of nitrogen-hydrogen pairs[8,9] (only one H interstitial is trapped per N atom[10]).

Our specific-heat data (temperature range: 0.07–1.5 K) were measured with a standard quasiadiabatic method,[11] using a dilution refrigerator. Magnetic fields were screened to less than 0.02 G. The samples consisted of spools (1 cm diameter, 4 cm length) wound from niobium wires (1.25 mm diameter, 80 cm length). Wire samples rather than bulk samples were used since (a) they are easy to purify (via Ohmic heating), (b) they provide high quenching rates (large surface to volume ratios) required to prevent nitrogen clustering after doping, and (c) their content of interstitial impurities (N, O, C) can reliably be controlled by residual-resistivity measurements.[12] At the same time, the spool-shaped samples had a dimension appropriate for our cryostat, and a mass (9 g) providing a sufficient experimental accuracy for specific-heat measurements (better than 5%).

For purification and nitrogen doping, the niobium wires (received with a purity of 99.99% according to the manufacturer, Materials Research Corporation) were first decarburized at 1500°C in an oxygen atmosphere of $10^{-5}$ mbar,[13] then annealed at 2200°C in a vacuum of $10^{-10}$ mbar, and, after being wound into a spool, once more annealed at 1800°C to remove cold-work dislocations. This final anneal was performed at $10^{-10}$ mbar for the nitrogen-free samples; the samples intended for nitrogen doping were exposed to appropriate $N_2$ pressures,[13] and, after doping, quenched to room temperature. The hydrogen loading was performed electrolytically (0.1% $H_2SO_4$ in $H_2O$ or $D_2SO_4$ in $D_2O$), and at room temperature, in order to prevent nitrogen clustering. All samples had less than 45 ppm of interstitial impurities (exclusive of H, D, or N for accordingly doped samples). The nitrogen concentrations (0.3 and 0.6 at.% for the doped samples) were determined by residual-resistivity measurements[12] (before hydrogen doping); the hydrogen concentrations (0.2 at.%, doped samples) were derived from the hydrogen-induced resistivity increase,[8,14,15] and by vacuum extraction from the amount of dissolved hydrogen after the measurements were completed.

Figure 1 shows the specific-heat data of our samples. Also indicated are results obtained by Sellers, Anderson, and Birnbaum,[2] and specific-heat values calculated for pure niobium. Our results demonstrate (a) that the pure niobium sample and the samples doped with *either* nitrogen or hydrogen have specific-heat values very close to those calculated for pure niobium, and (b) that the samples doped with ***both*** nitrogen and hydrogen show a very large and isotope-dependent anomaly in the specific heat. We conclude that the anomaly requires the presence of both nitrogen and hydrogen, and that it is caused by nitrogen-hydrogen pairs where the hydrogen tunnels among different trap sites.

According to the present result, hydrogen tunneling is very likely to occur also in the case of other trap centers like interstitial oxygen[6,7] or carbon.

The small specific-heat increase (with respect to the calculated values) observed for the pure niobium sample and for the samples doped with either nitrogen or hydrogen can be attributed to spurious contaminations with H, N, O, or C. It must be concluded that the specific-heat anomalies observed by Sellers, Anderson, and Birnbaum[2] also were caused by trapped hydrogen. Their samples had a residual-resistivity ratio of 100[17] indicating a content of interstitial nitrogen, oxygen, and carbon of about 0.035 at.%,[12] and a hydrogen content exceeding this concentration. The experiments represent, therefore, measurements with an amount of trapped hydrogen of about 0.035 at.%[10] which is about a factor of 6 smaller than that of our samples doped with both nitrogen and hydrogen (provided that O and C interstitials show a trapping behavior similar to that of nitrogen, which seems realistic at least in the case of oxygen[6,7]). The excess hydrogen which precipitates does not contribute to the specific-heat anomaly, as can be seen from our sample doped solely with hydrogen.

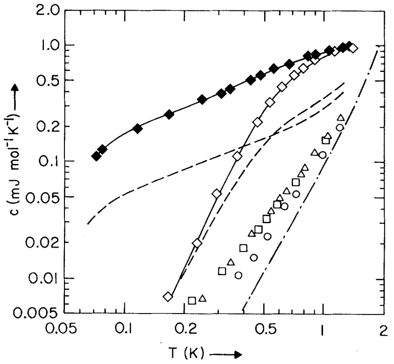

FIG. 1. Specific heat $C$ of (superconducting) Nb samples partially doped with H, D, and N, in a log-log plot vs temperature $T$. ○, pure Nb (residual-resistivity ratio = 1600); □, Nb-N(0.3 at.%); △, Nb-H(0.2 at.%); ◇, Nb-N(0.6 at.%)-H(0.2 at.%); ◆, Nb-N(0.3 at.%)-D(0.2 at.%). The solid curves are guides to the eye. The dashed curves indicate specific-heat data reported by Sellers, Anderson, and Birnbaum (Ref. 2) for niobium doped with H and D. The dash-dotted curve represents calculated specific-heat values for pure niobium (Ref. 16).

The fact that tunneling of trapped hydrogen rather than tunneling of free (untrapped) hydrogen within the $\alpha$ phase (as proposed in Ref. 5) causes the specific-heat anomaly is in agreement with the niobium-hydrogen phase diagram[8,18,19] according to which the amount of untrapped hydrogen in the $\alpha$ phase is, below 80 K, smaller than 1 ppm, thus being negligible within the present discussion. Further, the slow cooling rates of the specific-heat measurements prohibit any significant quenching of free hydrogen in the $\alpha$ phase as can be deduced from quenching experiments[9,19] on highly purified niobium.

A question which cannot be answered from the present experiment is that of the interstices occupied by the nitrogen-hydrogen tunneling pair. From reorientational relaxations observed in internal-friction experiments, suggestions have been made on possible sites for hydrogen trapped by oxygen or nitrogen[20,21] [e.g., hydrogen sites like $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ around an oxygen atom at $(\frac{1}{2},\frac{1}{2},0)$[20]]. Hydrogen tunneling can, therefore, be speculated to occur among these sites. A problem with such a model is the long relaxation times (up to 100 s[22]) found for the reorientation processes which make a tunneling among these sites not immediately understandable. This problem can be overcome by considering additional low-energy and tunnel-split trap sites, around a nitrogen atom, which are populated at low temperatures. Additional sites not yet detected by internal friction seem indeed realistic since the internal-friction experiments[20,21] themselves suggest already several types of trap sites. (The experiments performed at higher temperatures[21] indicate the occupation of a larger number of sites.) Another possibility is to assume that each of the trap sites observed by internal friction represents itself a system of tunnel-split sites as repeatedly proposed for untrapped hydrogen.[5,23]

A knowledge of the interstitial positions, and the use of appropriate tunneling matrix elements, should allow the calculation of the tunnel-split energy levels and, therefore, the observed specific-heat anomaly. However, any such calculation suffers from the fact that the size of the observed anomaly is considerably smaller than expected for concentrations of trapped hydrogen of 0.2 at.% (our data) or 0.035 at.% (Sellers, Anderson, and Birnbaum[2]). [Between 0.07 and 1.5 K, the entropy increase due to the specific-heat anomaly is $0.055k_B$ and $0.087k_B$ per trapped H and D atom for our data, and $0.11k_B$ (H) and $0.13k_B$ (D) for those of Ref. 2.] Such a discrepancy can result from nitrogen clustering or trapping at dislocations, which reduces the amount of tunnel-active traps; this effect should be of minor importance at least for our samples because of the sample-preparation technique applied. The discrepancy can, however, be attributed to stress-induced interaction effects among neighboring nitrogen-hydrogen pairs. Indeed, experiments on other tunneling systems[24] show that specific-heat data are severely affected, and reduced in size, by interaction effects for defect densities as large as the present ones (more than $10^{20}$ pairs/cm$^3$).

To estimate the size of the stress-induced interaction, we consider the energy splittings arising in a stress field for different orientations of a nitrogen-hydrogen pair (i.e., for differently oriented trap sites of one type occupied by the hydrogen). We calculate the energy splittings for a pair 1 in the stress field of the next-nearest-neighbor pair (pair 2) being a distance $r$ away, using continuum elasticity theory. For reasons of simplicity, we do not consider the influence of more distant pairs; further, we assume isotropic elastic moduli, and we disregard the elastic anisotropy of pair 2 (all these assumptions cause only an underestimation of the arising energy splittings). Considering two orientations $\alpha$ and $\beta$ of pair 1, the energy splitting $\Delta E$ can be written as[25]

$$\Delta E = \frac{9}{4\pi r^3}\frac{P(P_\alpha - P_\beta)}{3K+4\mu}, \tag{1}$$

where $K$ and $\mu$ are the bulk modulus and the shear modulus, respectively. $P$ is one-third the trace of the dipole-moment tensor of a nitrogen-hydrogen pair, and $P_\alpha$ and $P_\beta$ are, for the two orientations $\alpha$ and $\beta$, the trace components of the dipole-moment tensor of pair 1 in direction of the axis connecting the two pairs. In Eq. (1), the rapid decrease of $\Delta E$ with increasing $r$ justifies our limitation on interaction effects only among next-nearest-neighbor pairs. A representative value for the distance $r$ between next-nearest-neighbor pairs is given by[26]

$$r = 0.55 n^{-1/3}, \tag{2}$$

where $n$ is the number of pairs per unit volume.

From the equations above and dipole-moment tensor values reported from internal-friction experiments on trapped hydrogen[6,7] energy splittings up to about $10^{-3}$ eV can be estimated for our pair concentrations. (The dipole-moment tensor values are not necessarily representative for deuterium, or for hydrogen-tunneling sites different from those observed in internal friction; however, they may give an order-of-magnitude estimate also for these cases, for which better information is not yet available.) The calculated energy splittings reach values which correspond to temperatures larger than those at which the specific-heat anomalies are observed; their severe influence on the measured data is, therefore, understandable.[24] Finally, we note that, between 0.07 and 1.5 K, the entropy increase caused by the specific-heat anomaly is, per trapped hydrogen, larger (and less affected by interaction effects) in the experiments of Sellers, Anderson, and Birnbaum[2] than in our experiments, in which internal stresses were more severe due to higher trap concentrations.

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[1] For recent reviews, see J. Völkl and G. Alefeld, in *Diffusion in Solids*, edited by A. S. Nowick and J. J. Burton (Academic, New York, 1975); E. G. Maksimov and O. A. Pankratov, Usp. Fiz. Nauk 116, 385 (1975) [Sov. Phys. Usp. 18, 481 (1976)].

[2] G. J. Sellers, A. C. Anderson, and H. K. Birnbaum, Phys. Rev. B 10, 2771 (1974).

[3] L. Y. L. Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Lett. 14, 1025 (1965).

[4] G. Alefeld and H. Wipf, Fiz. Nizkikh Temp. 1, 660 (1975) [Sov. J. Low Temp. Phys. 1, 217 (1975)].

[5] H. K. Birnbaum and C. P. Flynn, Phys. Rev. Lett. 37, 25 (1976).

[6] C. Baker and H. K. Birnbaum, Acta Metall. 21, 865 (1973).

[7] P. Schiller, Nuovo Cimento 33B, 226 (1976).

[8] G. Pfeiffer and H. Wipf, J. Phys. F 6, 167 (1976).

[9] R. Hanada, in *Proceedings of the Second International Congress Hydrogen in Metals, Paris, 1977* (Pergamon, Oxford, 1977), Vol. 3, 1B6.

[10] For H concentrations exceeding those of nitrogen, the excess hydrogen precipitates. Note also that fast quenching can cause trapping of more than one H interstitial per N atom (Ref. 9).

[11] J. P. Harrison, Rev. Sci. Instrum. 39, 145 (1968).

[12] H. Schultz, Mater. Sci. Eng. 3, 189 (1968/69).

[13] E. Fromm and H. Jehn, Metall. Trans. 3, 1685 (1972).

[14] D. G. Westlake and S. T. Ockers, Metall. Trans. 6A, 399 (1975).

[15] W. Maier and H. Wipf, Scr. Metall. 11, 695 (1977).

[16] The lattice contribution of the specific heat was calculated using a Debye temperature of 274 K deduced from elastic-modulus measurements [G. A. Alers and D. L. Waldorf, Phys. Rev. Lett. 6, 677 (1961); R. Weber, Phys. Rev. 133, A1487 (1964)]. The small (superconducting-state) electronic contribution was derived from a low-temperature extrapolation of electronic specific-heat data measured above 2 K (Ref. 3) (above 2 K, the hydrogen-induced specific-heat anomaly becomes insignificant compared with the electronic contribution).

[17] The residual resistivity ratio of the Nb samples used by Sellers, Anderson, and Birnbaum (Ref. 2) is stated in S. G. O'Hara, G. J. Sellers, and A. C. Anderson, Phys. Rev. B 10, 2777 (1974).

[18] D. G. Westlake, Trans. AIME 245, 287 (1969).

[19] K. Faber and H. Schultz, Scr. Metall. 6, 1065 (1972).

[20] P. Schiller and H. Nijman, Phys. Status Solidi (a) 31, K77 (1975).

[21] R. F. Mattas and H. K. Birnbaum, Acta Metall. 23, 973 (1975).

[22] C. G. Chen and H. K. Birnbaum, Phys. Status Solidi (a) 36, 687 (1976).

[23] J. Buchholz, J. Völkl, and G. Alefeld, Phys. Rev. Lett. 30, 318 (1973).

[24] V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. 42, 201 (1970).

[25] H. E. Schaefer and H. Kronmüller, Phys. Status Solidi (b) 67, 63 (1975); Eq. (1) describes the difference in the defect interaction energy for the two orientations $\alpha$ and $\beta$ of pair 1; it is derived from Eq. (2.7) of this reference, under consideration of our simplifying assumptions.

[26] S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

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# Charge Density and Structural Properties of Covalent Semiconductors

H. Wendel and Richard M. Martin
*Xerox Palo Alto Research Center, Palo Alto, California 94304*

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We propose a practical scheme to calculate structural energies in crystalline semiconductors. The method is applied to Si to calculate changes in charge densities and harmonic energies for TO(Γ), TA($X$), and $C_{11}-C_{12}$ distortions. Cubic anharmonic terms are also found for TO(Γ). For the shear modes a proper description of the electron-electron interaction is found to be vital. Electronic charge densities demonstrate the importance of dynamic redistribution of valence charge in covalent semiconductors.

In this Letter we introduce a practical scheme to calculate the charge density and total energy of crystals as a function of atomic displacements. The method is not restricted to small displacements, and is here used to calculate directly from the electronic Hamiltonian both harmonic