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[15] Previously, the influence of self-interstitials as D traps has been ruled out mainly because the self-interstitials in fcc metals become mobile far below the temperature at which D depopulates the traps (Refs. 2–4) [annealing-state I_D for Ni = 56 K (Ref. 17)]. This argument is withdrawn by the explanation that a 0.24-eV binding of D to an interstitial greatly retards the migration of the latter. However, the high mobility of the interstitials may nevertheless influence the trapping-retrapping rate and thus the derived E_B value.

[16] Di-interstitials [parallel dumbbells on nearest-neighbor sites (Ref. 14)] is another possibility. The binding to di-interstitials will be slightly stronger than the binding to self-interstitials (see Fig. 1), but the trends will be the same.

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Hydrogen-Induced Glasslike Specific-Heat Anomaly in Superconducting Crystalline NbTi$_{0.05}$

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Low-temperature specific-heat measurements (0.06–2 K) on a superconducting polycrystalline NbTi$_{0.05}$ alloy show an anomaly in the presence of interstitial H and D (up to 3 at.%). The excess specific heat is roughly linear in temperature, indicating the existence of a glasslike low-energy excitation spectrum. The results raise the question as to what extent previously observed low-temperature anomalies in metallic glasses may be due to H contamination.

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Insulating, amorphous solids (glasses) exhibit low-temperature anomalies in their thermal and elastic properties.[1-4] The anomalies are generally accepted to represent an intrinsic and universal feature of the amorphous state, in particular since they were also found to exist in metallic glasses.[5-7] They can to some extent even quantitatively be described by a phenomenological two-state tunneling model[1-4,8,9] which does not, however, specify the microscopic nature of the tunneling entities. The model adequately predicts an essentially constant low-energy excitation spectrum required, for instance, for a specific-heat anomaly that is roughly linear in temperature as experimentally observed.

In this Letter, we present low-temperature (0.06–2 K) specific-heat measurements on a superconducting, polycrystalline (bcc) $NbTi_{0.05}$ alloy showing an essentially linear excess specific heat in the presence of H and D impurities (up to 3 at.%). The experiments indicate, therefore, the existence of a glasslike low-energy excitation spectrum which is roughly constant in the investigated energy range between ~10 and 400 μeV. They show further that the observed anomaly is essentially proportional to H (D) concentration, and that there are no pronounced isotopic differences between H and D.

The results of our experiments are compiled in Fig. 1. The figure shows the measured specific heat [Fig. 1(a)] and the excess specific heat exceeding the calculated phonon and electron contribution of the H- or D-free host metal[11] [Fig. 1(b)]. The data clearly indicate the existence of a large specific-heat anomaly for the H- or D-doped samples although a precise determination of its size is affected above ~1 K by the unknown effects of H (D) on the background specific heat (phonons and electrons) of the investigated alloy (above ~1 K, the background is of the same order of magnitude as the measured specific heat). For degassed $NbTi_{0.05}$ (several hours at 750 °C and a pressure below 10^{-6} mbar), the measured specific heat is close to the calculated value above ~0.2 K, whereas the small anomaly identifiable below ~0.2 K is attributable to a residual H contamination of about 100 at. ppm.

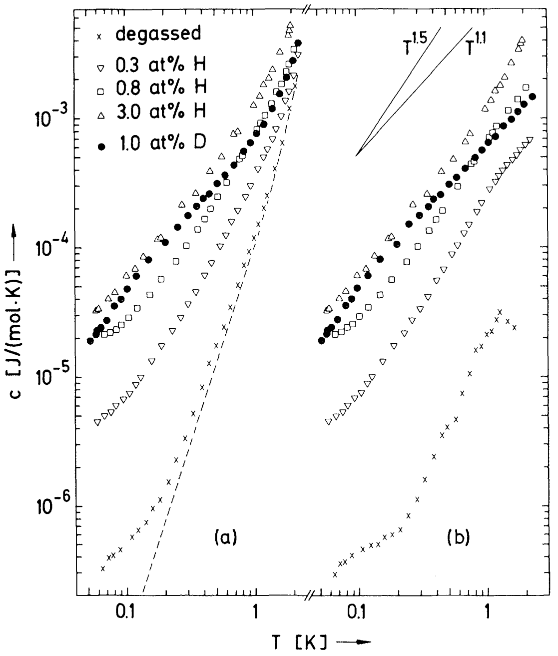

FIG. 1. (a) Measured specific heat and (b) excess specific heat of superconducting $NbTi_{0.05}$ doped with H and D. The broken line indicates the background specific heat (phonons and electrons) as calculated for pure Nb (Refs. 10 and 11) and the two solid lines indicate the slopes corresponding to a $T^{1.1}$ or $T^{1.5}$ dependence [see Eq. (1)].

According to Fig. 1(b), the excess specific heat per H (D) atom, c_{exc}, can be described by

$$c_{\text{exc}} = k_{\text{B}}\alpha T^{n}, \tag{1}$$

where k_{B} is Boltzmann's constant and T is the temperature. Fit results for the parameters α and n of the four H- or D-doped samples are given in Table I. The results for n (between 1.15 and 1.5) exceed somewhat the value $n = 1$ which indicates a deviation from a strictly linear temperature dependence similar to what is found in high-precision measurements on vitreous silica[4] ($n = 1.22$ and 1.30).

Important features of our results are as follows: (i) The size (per atom) of the anomaly is, depending on H (D) concentration, up to an order of magnitude larger than that typically found in both insulating and metallic glasses.[1,3-7] (ii) The high superconducting transition temperature (~9.3 K) enabled us to establish the temperature dependence of the anomaly over a wide range, in contrast to measurements on metallic glasses[6,7] where this range was restricted to temperatures below ~0.3 K (comparable to our degassed sample). (iii) H- or D-doped alloys, such as $NbTi_{0.05}$, may represent a model system for experimental studies on low-energy excitations characteristic for glasses since the responsible atomic species (H,D) is clearly identified and can substantially be varied in its isotopic mass, and since the excitation density is adjustable in a wide range by changing H (D) concentration. (iv) Our results finally indicate the possibility that previously observed glasslike low-temperature anomalies in metals may be due to the presence of H impuri-

TABLE I. Fit results for the parameters α and n [see Eq. (1)]. The experimental errors for α and n are 20% and 15%.

H (D) content	α (K^{-n})	n
0.3 at.% H	9.2×10^{-3}	1.5
0.8 at.% H	9.0×10^{-3}	1.3
3.0 at.% H	4.8×10^{-3}	1.35
1.0 at.% D	7.2×10^{-3}	1.15

ties. This holds in particular for the specific heat measurements[6,7,12-14] since the main constituents of the investigated alloys (Zr, Nb, Pd, La) exhibit—as do those of our sample—an extremely high affinity for H (Ref. 15) (in Nb, e.g., it is difficult to achieve a H contamination below ~100 at. ppm even under UHV conditions[16]), whereas it is possibly less evident for studies on alloys of lower H affinity such as Ni or Co phosphides.[5] (Note that H tunneling in amorphous Pd-Cu-Si alloys was also suggested from resistivity measurements between 4.2 and 300 K.[17])

We give now some experimental details. The $NbTi_{0.05}$ alloy (27 g), supplied by Materials Research Corp., had a total content of interstitial O, N, and C impurities of ~0.4 at.%. H (D) doping was performed by exposing the sample at ~650 °C to appropriate H_2 (D_2) gas pressure.[18] The resulting H (D) concentrations were controlled from the volume of the absorbed H_2 (D_2) gas, and from the H- or D-induced weight increase. The specific-heat data (experimental accuracy better than 5%) were taken with a standard quasiadiabatic method[19] in a dilution refrigerator.

According to the experimental technique applied, all energetic excitations relaxing thermally within a time period up to typically 50 s contributed to the measured specific heat. Below ~0.1 K, we observed substantial heat release from excitations relaxing on a much larger time scale, which, however, was difficult to assess quantitatively in view of our present experimental setup. In fact, this long-time heat release [found in glasses[20,21] and, incidentally, almost 20 years ago also in PdH_x (Refs. 22 and 23)] limited very effectively the lowest sample temperature we could reach in our experiments.

According to present knowledge, only a crude and speculative explanation can be given for the microscopic mechanism responsible for our observation of glasslike and H- or D-induced low-energy excitations in $NbTi_{0.05}$. Specific-heat,[24-26] thermal-conductivity,[27,28] and neutron-scattering[29] measurements show that tunneling eigenstates exist for H (D) in Nb at low temperatures if the H (D) is trapped by O or N impurity atoms, whereas tunneling is not observed for untrapped (free) H (D) which precipitates at low temperatures into an ordered hydride phase[25,26,30] [this explains also the moderate size of the effects reported in Refs. 24 and 27 since the concentration of trapped H (D) (~350 at. ppm[25]) was only a small fraction of the total H (D) content]. The results of those measurements can quantitatively be explained by H (D) tunneling between two tetrahedral trap sites that are randomly shifted against each other in their energetic levels because of strain fields from neighboring O or N defect atoms.[26,29,31]

It is tempting to apply a comparable tunneling concept to the present results. That Ti atoms in Nb represent effective trap centers for H (D) was shown in internal-friction studies,[32-34] and the trapped H (D) can therefore be considered to occupy tunneling systems which may consist of two or more interstitial sites[35] (the actual positions of these sites are not yet known). Because of electronic and elastic interaction effects with surrounding Ti atoms, the sites of a given tunneling system can again be expected to be severely and randomly shifted in their respective energetic levels. The existence of an essentially constant and isotope-independent excitation spectrum can then be explained in two ways: (i) We can assume that the relevant tunneling matrix elements for both H and D exhibit a broad distribution spectrum due to the lattice disturbances from neighboring Ti atoms. Such an explanation seems conceivable in view of the high Ti concentration in our sample, and it would particularly result in tunneling systems very close or even identical to those discussed for glasses[1-3,5,8,9] [distribution in both matrix elements (parameter Δ_0 in Refs. 2, 3, and 5) and energy shifts (Δ in Refs. 2, 3, and 5)]. (ii) The second explanation assumes that the relevant matrix elements (for both H and D) are smaller than the lowest energetic excitations probed in our experiments (~10 μeV). In this situation, the observed excitation spectrum would be due solely to the (essentially classical and isotope independent) energy shifts, and (quantum mechanical) isotopic differences due to tunneling would be effective only for excitation energies below 10 μeV.

A definite decision on which of the two explanations above is the more appropriate one requires further experimental investigation involving, for instance, specific-heat measurements on alloys containing less Ti (smaller interaction effects), or resonant phonon (thermal conductivity) and inelastic neutron scattering [in the relevant energy range between 10 and 400 μeV, both scattering processes are observable only for explanation (i), i.e., for tunneling matrix elements exceeding 10 μeV]. It is emphasized that we expect explanation (i)—essentially the standard tunneling model for glasses—to become the more appropriate the larger the disorder in the investigated alloy and, therefore, the larger the widths of the distribution spectra of matrix elements and energetic shifts. This means specifically that we expect H impurities in highly disordered metallic glasses to be very likely to represent a physical realization of the standard tunneling model.

In conclusion, our experiments have shown that H and D impurities in $\mathrm{NbTi}_{0.05}$ cause at low temperatures a glasslike excitation spectrum which is essentially constant in the investigated energy range between 10 and 400 μeV. Our results raise the question as to what extent previously observed low-temperature anomalies in amorphous or disordered metals may be due to H contamination.

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