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NMR studies of hydrogen motion in vacancies in Nb–H alloys

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Abstract

Proton NMR was measured in two Nb–H samples prepared so as to introduce vacancy–hydrogen (vac–H) clusters and a reference sample not containing vac–H clusters. A motionally narrowed signal persisting to very low temperatures was observed only in the former samples, and was assigned to protons executing a cage motion in Nb-atom vacancies. From the temperature dependence of the linewidth between 7 and 30 K, an apparent activation energy of 3.8 meV was deduced.

1. Introduction

Trapping of interstitial hydrogen in metals by metal-atom vacancies was studied intensively in the 1980s in connection with plasma–wall interactions in fusion-reactor research. Thus the binding energy was determined in many metals, a multiple occupancy (up to six H atoms per vacancy) was suggested, and trapped configurations distinct from those on regular interstitial sites were observed; see the review articles [1–4].

Subsequently, the formation of a large number of metal-atom vacancies amounting to as much as ∼10 at.% was discovered in Ni–H and Pd–H alloys, and explained in terms of reduction of the formation energy of a vacancy by trapping H atoms [5, 6]. The reduction can be significant: a reduction by the sum of binding energies of trapped H atoms can be comparable to the formation energy itself. This phenomenon, called superabundant vacancy (SAV) formation, has since been observed in a large number of metals, and its implications for many other physical properties have begun to be explored [7–22]. For a review, see [4].

The present paper is an attempt to characterize the quantum state of vac–H clusters. The only such work reported so far was on D in Ni, where a reversible change of the channelling

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profiles of implanted D atoms at low temperatures was interpreted in terms of thermal excitation between low-lying levels of D atoms in Ni vacancies [23]. In the present work, we aim at specifically investigating the motion of H atoms trapped by vacancies (the cage motion) at low temperatures, where the quantum-mechanical character is also expected to show up. For this purpose, the motional narrowing of proton NMR was measured in Nb–H alloys, in samples containing a small amount of vac–H clusters.

The Nb–H alloy is a convenient choice because, unlike most other cases, introduction of vac–H clusters does not require high temperatures or high hydrogen pressures, which allows the preparation of NMR samples without much difficulty. The process of SAV formation in Nb–H alloys was elucidated in our previous resistometric studies [22], where the equilibrium concentration and kinetics were determined under various conditions of H concentration, temperature, and pressure. The formation energy of a vac–H cluster was found to be $e_{\mathrm{f}}^{\mathrm{cl}} = 0.3 \pm 0.1$ eV, which is 1/10 of the formation energy of a vacancy in Nb ($e_{\mathrm{f}}^{\mathrm{v}} = 3.07$ eV [24]). The equilibrium concentration of vac–H clusters (x_{cl}) was found to be nearly proportional to the H concentration x; $x_{\mathrm{cl}} \approx 1.3 \times 10^{-2} x$ at 300 °C. Vacancy–H clusters were formed in two different time regimes: a fast process in $\leqslant$1 ks and a slow process typically over ~100 ks. From the dependence on sample size, the former was identified to be the process rate-controlled by short-circuit diffusion through dislocations, and the latter bulk diffusion from the surface. The former is dominant in polycrystals and the latter in single crystals. The activation energy of the fast process is 0.33 eV, and that of the slow process ~0.8 eV. On the basis of these pieces of information, it is possible to design techniques for preparing samples with and without vac–H clusters.

2. Experimental details

Samples were prepared by two different methods: $NbH_{0.08}$ and $NbH_{0.16}$ samples by slowly cooling in H_2 gas from high temperatures, and a $NbH_{0.15}$ sample by electrolytic charging at room temperature in 1N H_2SO_4. From what we learned from our previous studies [22], the former method is expected to introduce vac–H clusters, and the latter is not. In order to avoid extra broadening of proton NMR signals due to inhomogeneous distribution of demagnetizing fields, samples were assembled into a stack of 20 pieces of foil, 7 mm × 10 mm × 0.05 mm in size, interleaved with Teflon films to allow rf penetration [25, 26].

NMR measurements were made using a Bruker DSX-100 spectrometer operated at 44–48 MHz, in a cryostat either with liquid He or liquid N_2 during the natural warming up of the sample assembly in appropriate thermal contact with the coolant. Solid echo signals were repeatedly measured, accumulated, and Fourier transformed to give absorption-mode signals. The rf field strength was fixed at $H_1 \approx 20$ Oe, optimized for measuring motionally narrowed lines, but probably not large enough to tip the whole spins of the broad-line (rigid-lattice) component. For motionally narrowed lines, the linewidth was determined by fitting to a Lorentzian function.

3. Results

3.1. Observed features at $T \geqslant 77$ K

Proton NMR signals from the three samples observed at room temperature are shown in figure 1. The sharp lines observed in all the cases come from the α-phase and the broad (but partially narrowed) lines observed only for $NbH_{0.15}$ and $NbH_{0.16}$ come from the β-phase. (For the phase diagram of the Nb–H system, see [27].) The spin–lattice relaxation time of the sharp line component was $T_1 = 135$ ms, and that of the broad-line component $T_1 = 15$ ms.

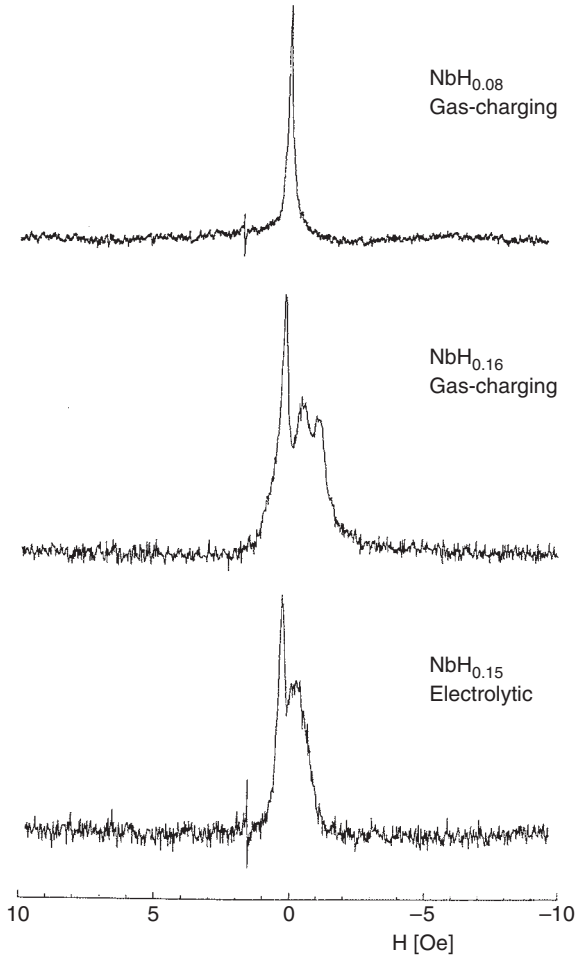

Figure 1. Proton NMR signals observed at room temperature for (a) $NbH_{0.08}$ and (b) $NbH_{0.16}$ prepared by gas charging, and (c) $NbH_{0.15}$ prepared by electrolytic charging. Measurements were made at 48 MHz, repeated 600 times every 1 s.

Figure 2 shows corresponding signals at 77 K. A notable feature is that a sharp line remains only for $NbH_{0.08}$ and $NbH_{0.16}$ prepared by cooling in H_2 gas. At this temperature, as the amount of the α-phase should be vanishingly small, what one would expect is a broad (rigid-lattice) signal from the β-phase, as was actually observed for $NbH_{0.15}$ and as a tail for gas-charged samples $NbH_{0.08}$ and $NbH_{0.16}$. A new feature here is the appearance of a narrow line only for the gas-charged samples. The presence of the narrow-line component for the gas-charged sample was also confirmed by cw measurements at 77 K; a weak but definitive signal was observed after accumulation of 500 times. The relaxation time of this narrow line was $T_1 = 1.8 \pm 0.2$ s. The concentration of hydrogen contributing to this narrow signal was roughly estimated at $\leqslant 2 \times 10^{-2}$ at 77 K. This is believed to be slightly overestimated because the intensity of the broad-line component (the β-phase signal), taken as a standard, should be underestimated due to insufficient H_1.

We presume that the narrow-line component observed at 77 K is due to protons executing a cage motion in Nb vacancies. Discussions leading to this assignment are given later.

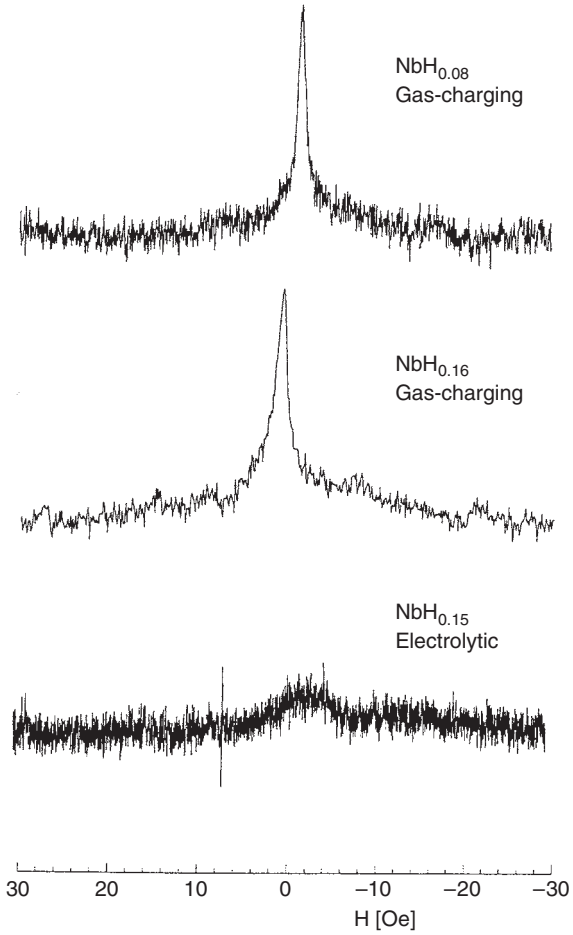

Figure 2. Proton NMR signals observed at 77 K for (a) $NbH_{0.08}$ and (b) $NbH_{0.16}$ prepared by gas charging, and (c) $NbH_{0.15}$ prepared by electrolytic charging. Measurements were made at 44 MHz, repeated 600 times every 6 s.

3.2. Temperature dependence of the linewidth

Narrow-line signals observed for $NbH_{0.08}$ at low temperature are shown in figure 3. Upon lowering the temperature, the linewidth starts increasing rapidly below ∼20 K. Very similar results were obtained for $NbH_{0.16}$. The overall temperature dependence of the linewidth (FWHM) is shown in figure 4. Apparently, the motional narrowing proceeds in two stages. Most probably, the first narrowing process below ∼30 K is due to excitation of the cage motion geometrically restricted in vacancies, and the second process above 160 K is due to the long-range migration in the α-phase.

4. Discussion

It is expedient here to start with the analysis of the narrowing process below ∼30 K. The mean jump time τ can be estimated from the relation (e.g. [28, 29])

$$\Delta H_{1/2}(\text{obs}) - \Delta H^0_{1/2} = \gamma \overline{\Delta H_L^2}\tau/\pi,$$

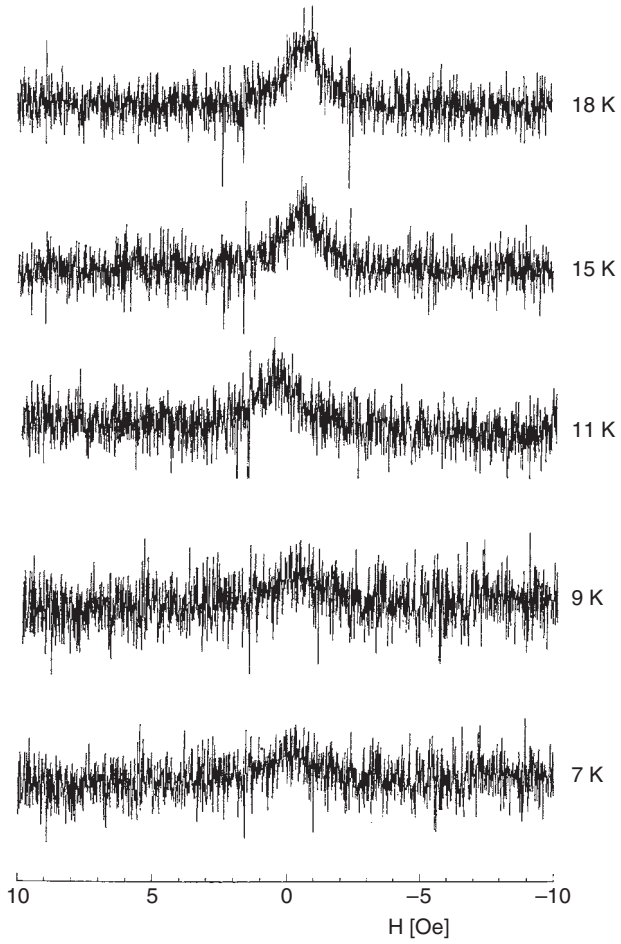

Figure 3. Motionally narrowed proton NMR signals observed in $NbH_{0.08}$ between 8 and 18 K. Measurements were made at 48 MHz, repeated 256 times every 2 s.

where $\Delta H^0_{1/2}$ is the residual width ($\Delta H^0_{1/2} = 0.8$ Oe), γ is the gyromagnetic ratio of the proton ($\gamma = 2.673 \times 10^4$), and $\overline{\Delta H_L^2}$ is the second moment of the proton at sufficiently low temperatures, approximately evaluated to be $\overline{\Delta H_L^2} \approx 35$ Oe^2; see the appendix.

The Arrhenius plot of the mean jump frequencies τ^{-1} obtained this way is shown in figure 5. Although the scatter of data is rather large, the temperature dependence is small, with an apparent activation energy of $e_a \approx 3.8$ meV.

A comparison of the jump frequency thus deduced with those for protons in other states in Nb is shown in figure 6. The observed jump frequencies are much smaller than those of protons in the α-phase [30], and in the 2T states formed in O–H pairs [31, 32]. In both cases, the jumps are known to occur by tunnelling between adjacent T sites. The frequency of reorientational motion of O–H pairs is, on the other hand, much lower than the observed jump frequencies [33–37]. The reorientational jumps are, in fact, too slow to cause motional narrowing at 77 K. Thus, even admitting the presence of some O–H pairs in our samples, they cannot be responsible for the narrow signals observed below 77 K.

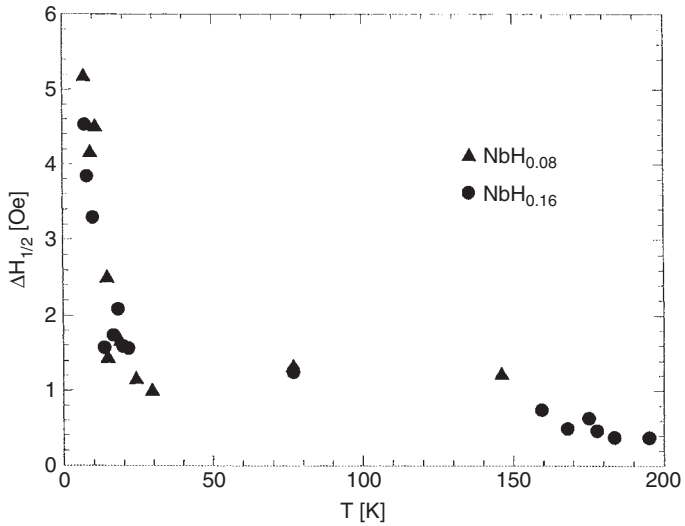

Figure 4. The linewidth (FWHM) of the motionally narrowed proton NMR signals of $NbH_{0.08}$ and $NbH_{0.16}$ as a function of temperature.

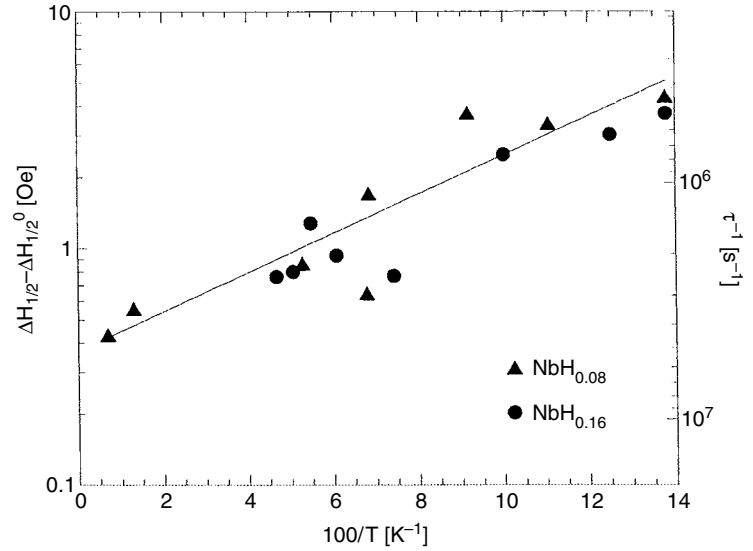

Figure 5. The Arrhenius plot of the mean jump frequencies deduced from the motional narrowing of proton NMR signals below ∼30 K.

Another possible concern that the narrow signal might be due to hydrogen bubbles can also be eliminated on the basis of the observed relaxation time: $T_1 \approx 2$ s is at least an order of magnitude longer than the relaxation time of fluid H_2 at corresponding temperatures [38, 39]. The magnitude of T_1 being comparable to what is expected from the Korringa relation in the α-phase ($T_{1e}T = 110$ s K [36]) suggests that the protons giving the narrow signal are embedded in the sea of conduction electrons.

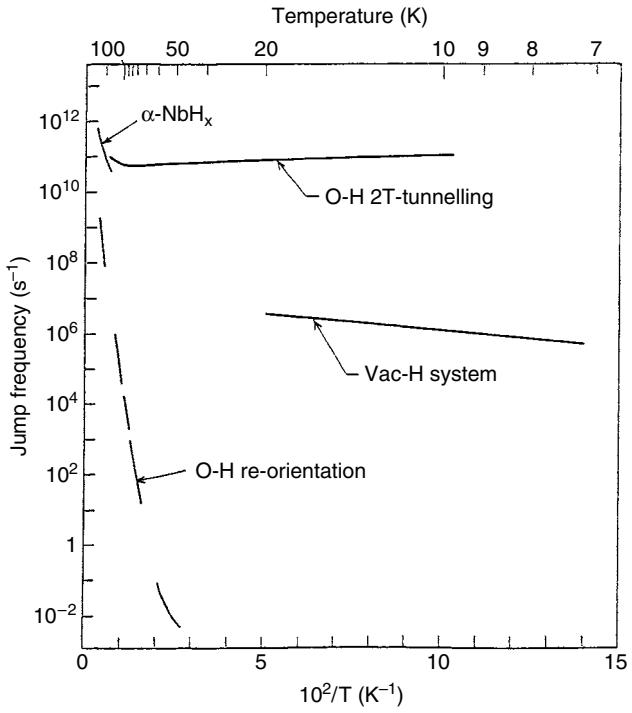

Figure 6. Comparison of jump frequencies of H atoms in several different states in Nb–H alloys. The jump frequencies in the α-phase were estimated from the long-range diffusion (Gorsky effect) [30], those for 2T tunnelling in O–H pairs from quasi-elastic neutron scattering [31, 32], those for reorientational motion of O–H pairs from internal friction [33–35] and NMR [36, 37].

A more definitive assignment of the narrow signal to protons trapped in vacancies can be made on the basis of the following observations. First, the narrow signal appeared only for gas-charged samples where the formation of vac–H clusters is expected. Second, the observed intensity ratio of 10^{-3}–10^{-2} is of the order of magnitude expected from our previous resistometric studies. Third, the temperature of the second narrowing process at $\sim$160 K is also roughly consistent with this assignment. Taking the ratio of this temperature to the annealing temperature of vacancies in Nb (190 K) [24], and substituting the known values of the migration energy of a vacancy ($e_{\mathrm{m}}^{\mathrm{v}} = 0.55$ eV [24]) and of an H atom ($e_{\mathrm{m}}^{\mathrm{H}} = 0.07$ eV [30]) into the approximate relation $(e_{\mathrm{b}} + e_{\mathrm{m}}^{\mathrm{H}})/e_{\mathrm{m}}^{\mathrm{v}} \approx 160/190$, we obtain the binding energy of $e_{\mathrm{b}} = 0.4$ eV. This value is consistent with an estimate from the observed formation energies of a vacancy and a vac–H cluster: assuming an occupancy of six H atoms in a vacancy, we obtain $e_{\mathrm{b}} \approx (e_{\mathrm{f}}^{\mathrm{v}} - e_{\mathrm{f}}^{\mathrm{cl}})/6 \approx 0.46$ eV. The binding energy deduced here is slightly smaller than $e_{\mathrm{b}} = 0.55$ eV [22] deduced from PAS experiments [40], but appears reasonable because the former refers to the state of multiple occupancy of H atoms in a vacancy whereas the latter refers to a single H atom in a vacancy. The average binding energy is expected to decrease for higher occupancies due to mutual repulsion between H atoms [41].

A mechanism of the cage motion can be envisaged, at least to some extent, on the basis of available information on the configuration of vac–H clusters. Ligeon *et al* [42] found by channelling experiments that D atoms implanted in Nb occupy T sites displaced by $\sim$0.2 Å towards nearest O sites (dis-T sites). This implies that, in a $\mathrm{vacH_6}$ cluster with a vacancy placed at the centre of a unit cube, each H atom occupies one of the four dis-T sites forming a

4T ring on a cube face, and the distance between the neighbouring 4T rings is ∼0.9 Å. If we assume in addition that these 4T rings are displaced towards a vacancy, by ∼0.3 Å (10% of the lattice constant) for example, the path length connecting the 4T rings on neighbouring cube faces becomes ∼1.0 Å. In consequence, these 24 dis-T sites form a cage around a vacancy, with mutual separations of $\leqslant$1.0 Å. Noting that these separations are comparable to the 2T distance in O–H pairs in Nb [43] and the intervening potential barrier should be reduced by the presence of a vacancy, we may expect the tunnel splitting between the neighbouring dis-T sites to become comparable to or even larger than 0.23 meV for the 2T state in O–H pairs [31, 44]. It is therefore very probable that the six H atoms distributed over these 24 dis-T sites may execute a cage motion via tunnelling transitions between neighbouring dis-T sites. Whether the six H atoms execute a consorted motion or move via metastable positions besides these dis-T sites is a question left for future studies. It is even conceivable that the six H atoms in a vacancy should be treated as a unified quantum-mechanical entity, an H_6 cluster embedded in the sea of conduction electrons. In any case, the state and motion of clusters of H atoms formed in M-atom vacancies are expected to pose a novel question of quantum-mechanical origin. The present work is a first step towards such an investigation.

5. Summary and conclusions

Using techniques of sample preparation for introducing vacancy–hydrogen clusters in Nb–H alloys, proton NMR signals motionally narrowed down to very low temperatures were observed and identified to be arising from protons executing a cage motion in Nb-atom vacancies. From the temperature dependence of the linewidth at 7–30 K, an apparent activation energy of 3.8 meV was deduced. A possible quantum character of this motion is suggested.

Acknowledgments

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Appendix

The expression for the second moment of the proton NMR in Nb–H alloys is given by [45]

$$\overline{\Delta H_{\mathrm{L}}^2} = 357 \sum_i r_i^{-6} + 313.5 \sum_j r_j^{-6} \ [\mathrm{Oe}^2],$$

where the first term comes from the H–H interaction and the second term from the H–Nb interaction, with r_i and r_j representing H–H and H–Nb distances (in Å), respectively.

In order to evaluate $\overline{\Delta H_{\mathrm{L}}^2}$ in the present problem, we need to know the configuration of $\mathrm{vac}H_6$ clusters—more specifically the position and extent of the wavefunction of six protons distributed over 24 dis-T sites. In the absence of this knowledge, we performed the approximate evaluation on the basis of the following simplified model.

We note that a strong constraint on the distribution of protons is imposed by the mutual repulsion acting between the protons. In view of this, we expect that no two neighbouring dis-T sites are occupied simultaneously, not even two dis-T sites belonging to the same 4T ring. This situation can be incorporated approximately in the second-moment calculation by simply

placing a proton at the centre of each 4T ring, i.e. at the O site. The presence of a vacancy at the centre of a cube should tend to pull the protons inward, but the displacement should also be limited by the mutual repulsion. Here we assume the displacement of 0.25–0.30 Å, which makes the distance between nearest O sites 1.98–1.91 Å, barely permissible from the minimum-distance criterion of 2.1 Å.

The use of these values (together with the lattice constant of Nb, 3.30 Å) gives the following second moment: for the displacement of 0.25 Å,

$$\overline{\Delta H_{\mathrm{L}}^2} = 24.4 + 7.5 = 31.9\ [\mathrm{Oe}^2],$$

and for 0.30 Å,

$$\overline{\Delta H_{\mathrm{L}}^2} = 31.4 + 7.4 = 38.8\ [\mathrm{Oe}^2],$$

the first values from the H–H interaction and the second values from the H–Nb interaction. In the analysis of the observed motional narrowing, we adopted the average of these values, $\overline{\Delta H_{\mathrm{L}}^2} = 35\ \mathrm{Oe}^2$. (Incidentally, this value coincides with the case of T-site occupancy in Nb [45].) To what extent this value corresponds to the actual situation is not easy to assess. Its sensitivity to the local cluster configuration as noted above indicates that it may be off by a factor of 2. This provides a crude measure of the reliability of the estimated jump frequencies.

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