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Proton NMR study of the lowest-hydrogen-content molybdenum bronze $H_{0.26}MoO_3$

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Temperature and frequency dependences of proton spin-lattice relaxation time have been measured in the lowest-hydrogen-content molybdenum bronze $H_{0.26}MoO_3$ by pulsed NMR method. Temperature dependence of proton NMR spectra have been also observed. It is revealed that protonic motion becomes active above about 165 K and the fluctuation of dipolar interaction of protons arising from the protonic motion governs the spin-lattice relaxation in the temperature range between 213 and 333 K. The activation energy is determined to be 1.30×10^4 J/mol and the correlation time τ_c is 1.29×10^{-8} s at room temperature. The protonic motion governing the spin lattice relaxation is discussed and it is suggested that the protonic motion is lattice diffusion. The diffusion constant D is estimated to be 3.27×10^{-12} m^2/s.

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INTRODUCTION

Molybdenum bronzes are formed by intercalating hydrogens or metal ions into molybdenum trioxide MoO_3, and are of interest not only from academic points of view such as unusual electrical conductivity and charge density wave and so on, but also in technical applications such as secondary battery electrodes, reversible hydrogen storage cells, hydrogen-transfer catalysts, and so on. Hydrogen molybdenum bronze H_xMoO_3 is a hydrogen insertion compound of molybdenum trioxide and, as is well known, exhibits four types of phases with the homogeneity of approximate limits;[1–5] Type I (blue orthorhombic, $0.21<x<0.40$), Type II (blue monoclinic, $0.85<x<1.04$), Type III (red monoclinic, $1.55<x<1.72$), and Type IV (green monoclinic, $x=2.0$). Recently, a new type of hydrogen molybdenum bronzes, Type II′ (blue monoclinic, $0.25<x<0.6$), has been discovered[6,7] in addition to these four types.

The location and mobility of hydrogens in hydrogen molybdenum bronzes have been investigated by inelastic neutron scattering,[8–12] neutron diffraction,[8,13,14] and NMR.[15–23] Among the NMR researches, precise studies of the location and mobility of protons in types I, II, III, and IV of hydrogen molybdenum bronzes were done by Slade, Halstead, and Dickens[18] and Ritter and co-workers[19,20] by measuring the temperature dependences of NMR spectra and spin-lattice relaxation times T_1 of protons by both continuous-wave and pulsed-NMR spectroscopies. Their studies, however, lacks the temperature dependence of proton T_1 in the lowest hydrogen content bronze (type I), because measurements by pulsed spectroscopy were prevented by extraordinary low content of inserted hydrogens. It is, therefore, worthwhile to compensate the lack with new data, in order to investigate this bronze in more detail. In the present work, we have succeeded to measure the temperature and frequency dependences of proton spin-lattice relaxation time T_1 in type I bronze $H_{0.26}MoO_3$, which, to our knowledge, have not yet been measured, by using a high sensitive pulsed-NMR spectrometer, which was designed and produced mainly by THAMWAY and partly by the present authors, and signal accumulation, and obtained the detailed data. We wish to report these data and theoretical analyses for them.

EXPERIMENT

The hydrogen molybdenum bronze $H_{0.26}MoO_3$ was prepared by the method described previously.[5] It was confirmed by the x-ray diffraction and chemical analysis that the prepared sample has a single phase. The sample comprised powders and were sealed in a glass tube to prevent decomposition.

Proton NMR was detected by a pulsed-NMR spectrometer operating at 9–27 MHz. The spin-lattice relaxation time was measured by applying 180°-τ-90° pulse sequence, and signals were accumulated up to 512 scans and averaged to improve the signal-to-noise ratio. Single exponential behavior of the proton NMR signals was observed after the 180° pulse in all temperature and frequency ranges. NMR spectra were observed by Fourier transform of the solid echo signal[24] following a 90_x-90_y pulse sequence, in order to avoid the distortion of the free induction decay signal owing to the lack of its initial part during the dead time of the receiver after an intense rf 90° pulse.

RESULTS

The temperature dependence of proton spin-lattice relaxation time in type I bronze was measured at 11 MHz. The spin-lattice relaxation rate $1/T_1$ is plotted as a function of $1000/T$ in Fig. 1. When the temperature is increased, the spin-lattice relaxation rate $1/T_1$ increases and has a maximum at 303 K, and decreases above 303 K. It again increases abruptly above 333 K.

The frequency dependence of the proton spin-lattice relaxation time in type I bronze was measured at room temperature 293 K and is presented in the spin-lattice relaxation rate $1/T_1$ as a function of frequency in Fig. 2. As increasing frequency, the spin-lattice relaxation rate $1/T_1$ simply decreases.

The temperature dependence of the proton NMR spectra

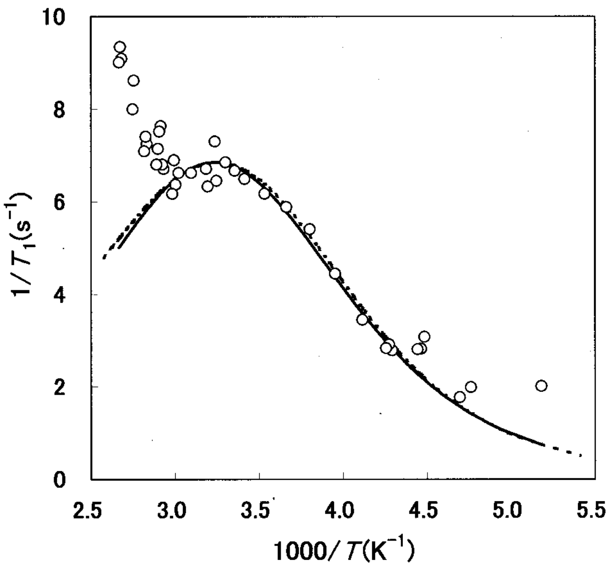

FIG. 1. Temperature dependence of proton spin-lattice relaxation rate $1/T_1$ measured at 11 MHz in type I bronze. Open circles are the experimental data, a solid curve is the theoretical one obtained from Eq. (3) and a dotted curve the theoretical one obtained from Eq. (8).

are shown in Fig. 3. At low temperatures they show well-resolved structures, but as increasing temperature the structure vanishes and the spectra become narrower.

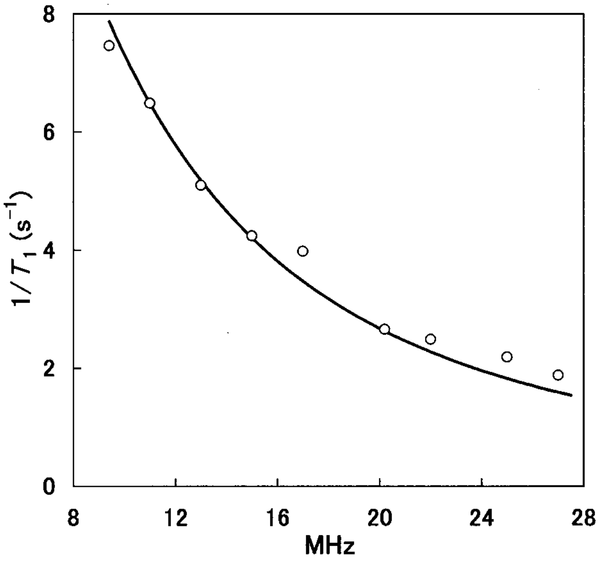

FIG. 2. Frequency dependence of proton spin-lattice relaxation rate $1/T_1$ measured at 293 K in type I bronze. Open circles are the experimental data and a solid curve is the theoretical one obtained from Eq. (5).

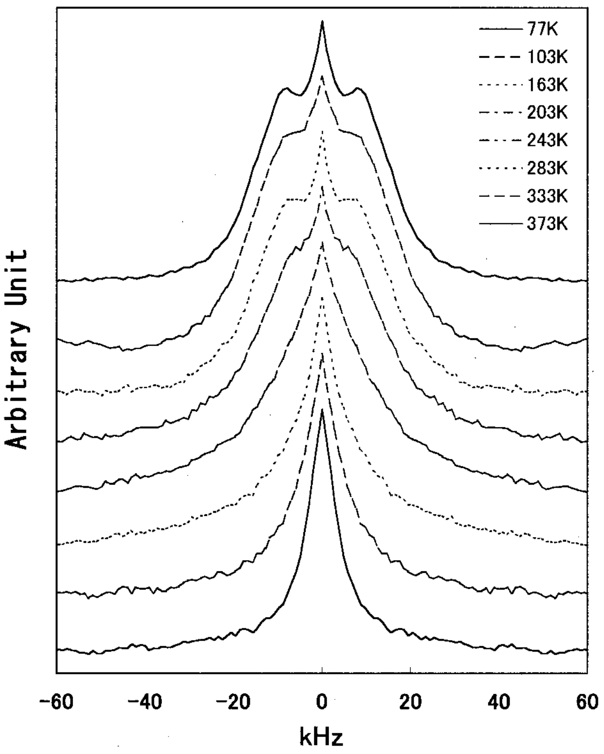

FIG. 3. Temperature dependence of proton NMR spectra in type I bronze.

ANALYSIS

The fact that the temperature dependence of spin lattice relaxation rate has a maximum is characteristic of the relaxation caused by the fluctuation of dipolar interaction arising from protonic motion.

The effect of dipolar interaction between proton spins and molybdenum spins (^{95}Mo and ^{97}Mo) to the proton spin-lattice relaxation can be ignored as follows. In order to estimate the contribution of molybdenum spins, one should compare the factor $\gamma_{\mathrm{Mo}}^2 I_{\mathrm{Mo}}(I_{\mathrm{Mo}}+1)N_{\mathrm{Mo}}/r_{\text{Mo-H}}^3$ with the similar factor for protons $\gamma^2 I(I+1)N/r^3$ (Refs. 25 and 26) where γ_{Mo} is the gyromagnetic ratio of molybdenum, I_{Mo} molybdenum spin, N_{Mo} the density of molybdenum spins per unit volume and $r_{\text{Mo-H}}$ is the minimum distance between a molybdenum and a proton in a unit cell, and other variables without subscripts are for proton spins. The contributions from both isotopes of molybdenum are estimated to be two or three order of magnitude smaller than that from protons (3.5×10^{-2} for ^{95}Mo and 6.1×10^{-3} for ^{97}Mo), by utilizing molybdenum gyromagnetic ratios (in a static magnetic field 1 T, resonance frequencies are 2.774 MHz and 2.833 MHz for ^{95}Mo and ^{97}Mo, respectively), their natural abandances (15.78 and 9.6 % for ^{95}Mo and ^{97}Mo, respectively), their spin (both $\frac{5}{2}$), and the minimum distance between a proton and a molybdenum (0.234 nm).

The relaxation rate caused by the fluctuation of dipolar interaction is represented as[25,26]

$$\frac{1}{T_1}=\frac{9}{8}\gamma^4\hbar^2\{J^{(1)}(\omega_0)+J^{(2)}(2\omega_0)\}, \tag{1}$$

for proton spin $\frac{1}{2}$, where γ is the gyromagnetic ratio of proton, and $J^{(1)}(\omega_0)$ and $J^{(2)}(2\omega_0)$ are the spectral densities. Assuming an exponential correlation function as

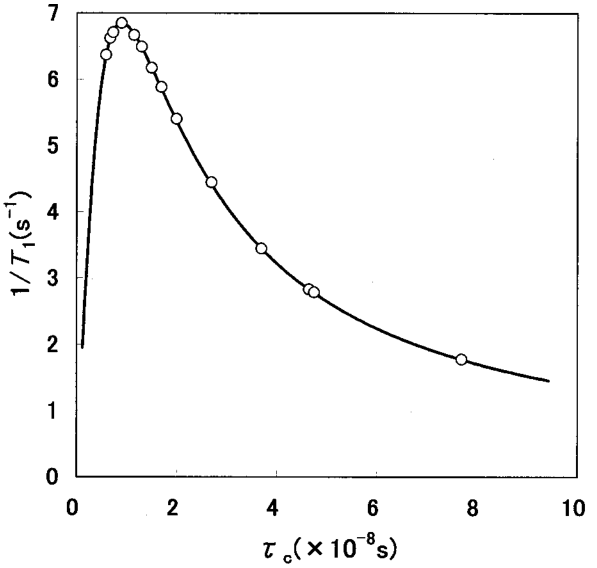

FIG. 4. Theoretical τ_c dependence of proton spin-lattice relaxation rate $1/T_1$ obtained from Eq. (3) in type I bronze and experimental data (open circles) fitted to it.

$$\exp\left(-\frac{|t|}{\tau_c}\right),$$

where τ_c is the correlation time, the relaxation rate becomes

$$\frac{1}{T_1}=C\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right], \tag{2}$$

where the relaxation strength C depends on the types of motions such as rotation, translation, and so on. The Eq. (2) has a maximum at $\omega_0\tau_c=0.616$. The present data were measured at $\omega_0=2\pi\times 11.00\,\mathrm{MHz}$, which gives $\tau_c=8.92\times 10^{-9}\,\mathrm{s}$ at the temperature, where the spin-lattice relaxation rate takes a maximum. As the spin-lattice relaxation time T_1 measured in the present experiment has a minimum 146 ms at 303 K, where the relaxation rate $1/T_1$ is maximum, the relaxation strength C can be determined to be $3.32\times 10^8\,\mathrm{s}^{-2}$ from Eq. (2). Using thus determined C, we obtain the τ_c dependence of the relaxation rate of protons in type I bronze as

$$\frac{1}{T_1}=3.32\times 10^8\left[\frac{\tau_c}{1+(2\pi\times 11\times 10^6)^2\tau_c^2}+\frac{4\tau_c}{1+4(2\pi\times 11\times 10^6)^2\tau_c^2}\right]. \tag{3}$$

The theoretical curve obtained from Eq. (3) is shown in Fig. 4. By fitting the measured data at each temperature to the corresponding point of this curve (open circles), the correlation time τ_c can be determined at each temperature.

The correlation times determined this way are plotted in ln τ_c versus inverse temperature $1000/T$ in Fig. 5. These are just on a straight line in the temperature range from 213 to 333 K. This fact leads us to the temperature dependence of the correlation time τ_c described by Arrhenius relation

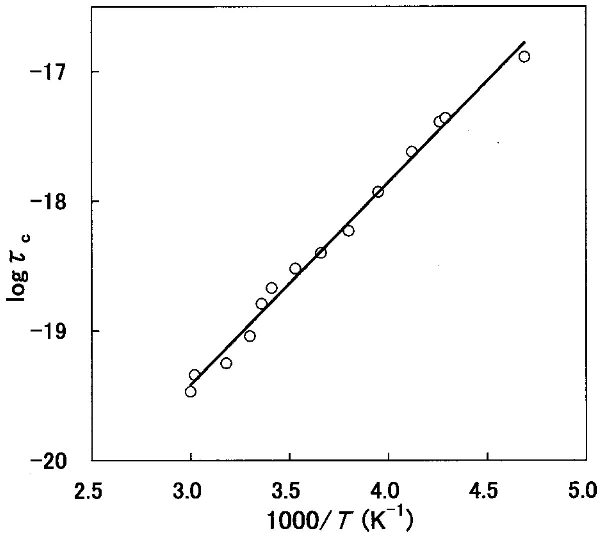

FIG. 5. ln τ_c as a function of inverse temperature $1000/T$.

$$\tau_c=\tau_{c0}\exp\left(\frac{E_A}{RT}\right), \tag{4}$$

where E_A is the activation energy of the motion, τ_{c0} is called the preexponential factor, which is the correlation time in the infinite temperature and R is the gas constant. By utilizing the least square method, we determined the activation energy and the preexponential factor to be $E_A=1.30\times 10^4$ J/mol and $\tau_{c0}=5.63\times 10^{-11}$ s, respectively.

In Fig. 1, the theoretical result (3) substituted for τ_c from Eq. (4) with the values $E_A=1.30\times 10^4$ J/mol and $\tau_{c0}=5.63\times 10^{-11}$ s is plotted together with the experimental data. Agreement between the measured data and the theoretical curve is satisfactory in the temperature range from 213 to 333 K.

The frequency dependence was measured at 293 K at which temperature the correlation time has been determined to be $\tau_c=1.29\times 10^{-8}$ s by the method mentioned above. Thus the theoretical frequency dependence of the relaxation rate is described as

$$\frac{1}{T_1}=3.32\times 10^8\left[\frac{1.29\times 10^{-8}}{1+\omega_0^2(1.29\times 10^{-8})^2}+\frac{4\times 1.29\times 10^{-8}}{1+4\omega_0^2(1.29\times 10^{-8})^2}\right]. \tag{5}$$

The theoretical curve obtained from Eq. (5) together with the measured data are shown in Fig. 2. Agreement between them is also satisfactory.

DISCUSSION

The temperature dependence of proton spin-lattice relaxation time in type I bronze suggests that, in the temperature range from 213 to 333 K, the relaxation mechanism is the fluctuation of the dipolar interaction between protons arising from protonic motion. This is confirmed also by the frequency dependence of the relaxation time. The activation

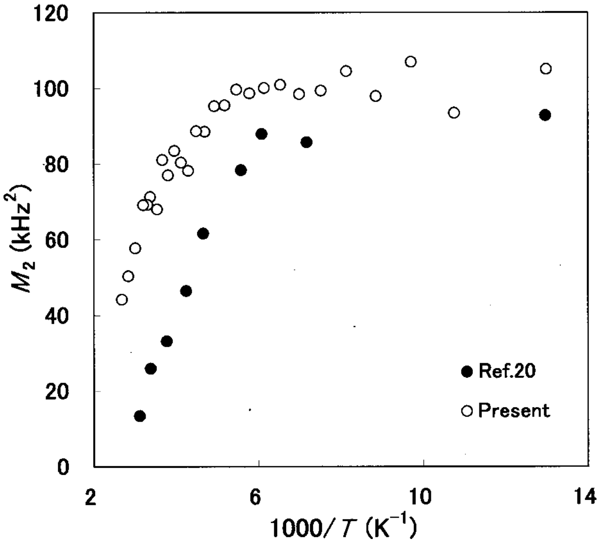

FIG. 6. Temperature dependences of proton second moment M_2 in type I bronze obtained by Ritter, Müller-Warmuth, and Schöllhorn (Ref. 20) (solid circles) and the present work (open circles).

energy was determined by Slade, Halstead, and Dickens[18] and Ritter and co-workers[19,20] respectively. The former was $E_A = 1.10\times 10^4$ J/mol determined by the spin-spin relaxation time, and the latter was $E_A = 2.67\times 10^4$ J/mol decided by applying qualitative formula to the temperature dependence of second moment of proton line shape. In the present experiment $E_A = 1.30\times 10^4$ J/mol was obtained, which is consistent with that obtained by Slade, Halstead, and Dickens and is half of that obtained by Ritter and co-workers *et al.* The present determination is rather quantitative than those by Slade, Halstead, and Dickens and Ritter and co-workers.

As shown in Fig. 3, the proton NMR spectra at 77, 103, and 163 K exhibit well-resolved structure having three peaks, as reported by Ritter and co-workers[19,20] and the present authors,[21,22] which originate in multiple proton clusters.[23] As we increase temperature above 203 K, the spectra become narrower and the structure disappears, having a single peak. This suggests that the protonic motion becomes active in these temperature range. The temperature dependence of the second moment M_2 were obtained from these spectra, as shown in Fig. 6, in which those measured by Ritter and co-workers[19,20] are also plotted together. Both data indicate that M_2 remains almost constant below 165 K and decreases with increasing temperature. From the temperature dependences of spin-lattice relaxation time and NMR spectra, it could be concluded that the protonic motion becomes active above about 165 K and effective on the proton spin-lattice relaxation in the temperature range from 213 to 333 K.

In order to decide a sort of protonic motion, it is necessary to examine the relaxation strength C. Torrey,[28] Wolf,[29] and Sholl[30] treated the spin-lattice relaxation caused by translational diffusion. They calculated the relaxation rates for the cases of isotropic diffusion and lattice diffusion by using the random-walk model. Among them, the studies of Wolf and Sholl correspond to the cases of high- and low-frequency limits, which are not in the present case. Then we wish to refer to the results of Torrey's calculation as follows for spin $I=\frac{1}{2}$.

(1) For the isotropic diffusion in the case of long mean flight path, the relaxation rate is

$$\frac{1}{T_1} = C_{\mathrm{id}}\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right], \tag{6}$$

where

$$C_{\mathrm{id}} = \frac{2\pi}{5}\,\frac{\gamma^4\hbar^2 N}{d^3}, \tag{7}$$

d is the minimum distance of approach of nuclei and N the density of spins per unit volume.

(2) For the lattice diffusion, it is

$$\frac{1}{T_1} = \frac{6\pi}{5}\,\gamma^4\hbar^2\frac{N}{k^3 l^3\omega_0}\,\Psi(k,\omega_0\tau_c), \tag{8}$$

where $k=d/l$, l is a jumping magnitude, and

$$\Psi(k,\omega_0\tau_c) = \omega_0\tau_c G(k,\omega_0\tau_c) + 2\omega_0\tau_c G(k,2\omega_0\tau_c), \tag{9}$$

$$G(k,\omega_0\tau_c) = \int_0^\infty B_{3/2}^2(kz)\,\frac{1-\sin z/z}{(1-\sin z/z)^2+\omega_0^2\tau_c^2}\,\frac{dz}{z}, \tag{10}$$

and $B_{3/2}$ is the Bessel function.

We applied these Torrey's results in the present study.

(1) We first tried to apply the relaxation strength for the isotropic diffusion. Substituting $d=0.16$ nm and $N=5.10\times 10^{27}$ m^{-3}, where N was estimated according to the unit cell volume ($a\times b\times c$, where $a=3.88\times 10^{-10}$ m, $b=1.41\times 10^{-9}$ m, and $c=3.73\times 10^{-10}$ m)[8] and the number of protons in the unit cell ($4\times x$, where 4 is the possible number of hydrogen sites[8] in an unit cell and $x=0.26$), into Eq. (7), we obtained the relaxation strength $C_{\mathrm{id}}=9.01\times 10^8$ s^{-2} for the isotropic diffusion. Obtained C_{id} is larger than the value $C=3.32\times 10^8$ s^{-2} determined from the present experiment.

(2) It should be natural, of course, in the hydrogen molybdnum bronze that the protonic diffusion is like one dimensional rather than isotropic. We applied Torrey's second result for the lattice diffusion to the present case; The τ_c dependence of spin-lattice relaxation rate was calculated by using Torrey's result in such a way that the maximum value was fitted to the observed maximum, and is shown in Fig. 7. As before, by fitting the measured data (open circles) to the corresponding point of this curve, one can determine the correlation time at each temperature. Correlation times determined this way are plotted logarithmically as a function of inverse temperature in Fig. 8. These are on a straight line in the temperature range from 213 to 333 K as before. Assuming Arrhenius relation and utilizing the least square method, the activation energy, and the preexponential factor were determined to be 1.35×10^4 J/mol and 4.41×10^{-11} s, respectively, which fairly agree with those obtained before. Equation (8) is also plotted in Fig. 1 (a dotted curve) by using the parameter obtained, together with the measured data. There is only a slight difference between the curves of Eq. (3) (the solid curve) and Eq. (8) (the dotted curve).

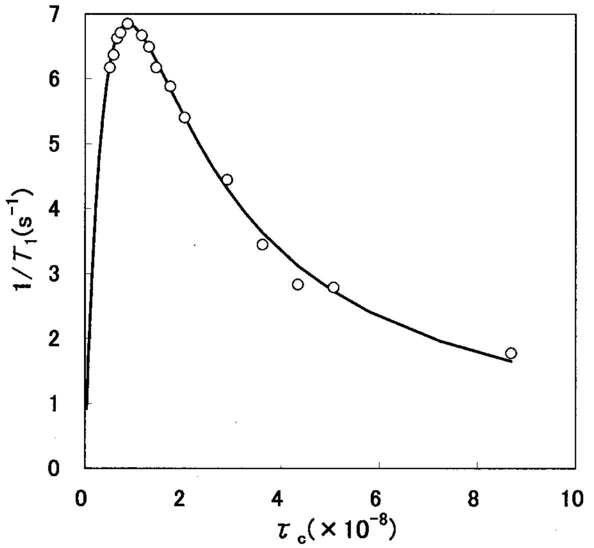

FIG. 7. Theoretical τ_c dependence of proton spin-lattice relaxation rate $1/T_1$ in type I bronze [after Torrey (Ref. 28)].

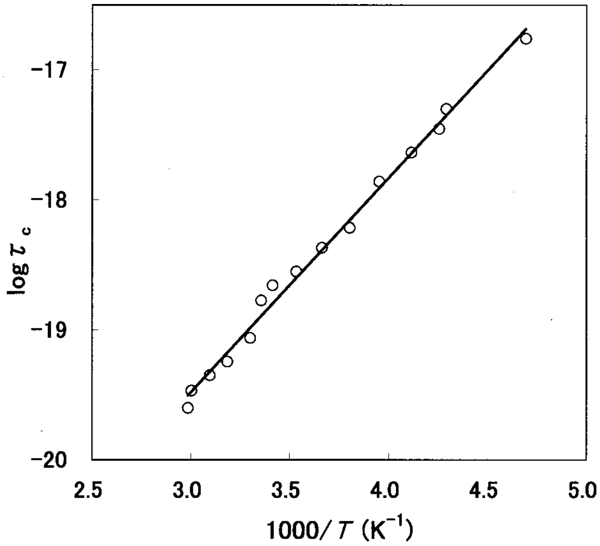

FIG. 8. ln τ_c as a function of inverse temperature 1000/T (after Torrey).

We estimated the diffusion constant D at room temperature (293 K) from the well-known relation

$$D=\frac{a^2}{2m\tau_c}, \tag{11}$$

where a is the jump distance and m equals 1, 2, or 3 depending on the dimensionality of the motion. By taking $a=0.28\,\mathrm{m}$ defering to Ritter, Müller-Warmuth, and Schöllhorn[20] and taking $m=1$ according to one dimensional motion of protons in type I bronze, and using $\tau_c=1.29\times10^{-8}$ s obtained in the present experiment, we obtained $D=3.27\times10^{-12}\,\mathrm{m}^2/\mathrm{s}$. Ritter, Müller-Warmuth, and Schöllhorn estimated the diffusion constant in the hydrogen molybdenum bronzes.[20] Their value for type I bronze $H_{0.35}MoO_3$ is $D=6.3\times10^{-12}\,\mathrm{m}^2/\mathrm{s}$, which is larger than ours. The diffusion constant estimated by Ritter, Müller-Warmuth, and Schöllhorn is largest for type III bronze $H_{1.0}MoO_3$ in the bronzes and decreases as both decreasing and increasing the content x. Our result is consistent with the results of Ritter, Müller-Warmuth, and Schöllhorn.

From these considerations, it may be concluded that the protonic motion is the lattice diffusion in the lowest hydrogen content molybdenum bronze, and is such that protons are hopping from one possible site to another which lies on the zigzag line connecting the vertex sharing oxygen atoms in the intralayers.

The measured points of the temperature dependence of proton spin lattice relaxation rate in $H_{0.26}MoO_3$ deviate from the theoretical curve obtained from Eq. (3) in the temperature range above 333 K as shown in Fig. 1. Other mechanisms than the fluctuation of dipolar interaction must be dominant to the proton spin-lattice relaxation in the temperature range above 333 K, where the spin-lattice relaxation rate shows an abrupt increase with increasing temperature. Adams, Ehses, and Spilker investigated type I hydrogen molybdenum bronze by electrical conductivity measurement. They observed a metal to semiconductor transition at between 375 and 415 K depending on the hydrogen content.[27] Then the abrupt change in spin lattice relaxation rate may accompany the phase transition and there is a possibility that the relaxation mechanism of proton at high temperatures is attributed to the interaction between proton spins and s-state conduction electron spins i.e., the contact interaction. If the contact interaction would govern the spin-lattice relaxation in the high-temperature range, Korringa relation $T_1T=\mathrm{const}$ can be applied to the temperature dependence of spin lattice relaxation time.[31] It seems, however, that Korringa relation could not be applied to the present data in the temperature range above 333 K. In order to confirm this discussion, further precise investigations must be made in the higher-temperature range including the transition temperature.

CONCLUSION

The temperature and frequency dependences of proton spin-lattice relaxation time in the lowest-hydrogen content molybdenum bronze $H_{0.26}MoO_3$ could be measured by using the high-sensitive pulsed-NMR spectrometer and the signal accumulation method. Proton NMR spectra were also observed and the temperature dependence of second moment was obtained. By analyzing these data it is concluded that the protonic motion becomes active above about 165 K and the proton relaxation mechanism is the fluctuation of the dipolar interaction between protons caused by protonic lattice diffusion in the temperature range from 213 to 333 K. The activation energy was determined to be 1.30×10^4 J/mol and the correlation time τ_c is 1.29×10^{-8} s at room temperature. The diffusion constant was estimated to be $3.27\times10^{-12}\,\mathrm{m}^2/\mathrm{s}$.

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