Rattling motion of ^{140}Ce($\leftarrow^{140}$La) confined in the hexaboride cage

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Rattling motion of the probe ^{140}Ce($\leftarrow^{140}$La) confined in the B cage of LaB_6 was observed by means of the time-differential perturbed angular correlation technique. The time scale of the motion is in the order of 10^{-11}-10^{-10} s at room temperature. The activation energy of the slow motion at higher temperatures (160 to 773 K) was deduced to be E_a=21.3(8) meV. At lower temperatures down to 10 K, a transitive state to motional freezing of the rattling was evidently observed, but the motion is still active for 76(2)% of the probe ions at this low temperature.

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I. INTRODUCTION

Lanthanum hexaboride (LaB_6), with a unique cryptoclathrate structure as shown in Fig. 1, has long been applied as a thermionic electron-emitting material because of its unique physical properties such as low work function and low vapor pressure. In addition to the practical use, this compound has attracted much attention to its unusual physical properties at low temperature such as specific heat and resistivity.[1,2] It has been pointed out that a model of local dynamic motion of La atoms as harmonic Einstein oscillators confined in a rigid Debye framework of B atoms well explains the anomalous behaviors,[2] and such vibrational motion of La atoms has been observed by means of proton channeling,[1] x-ray crystallography,[2] neutron inelastic scattering,[3] and so forth. In order to further understand physical properties of the inclusion compound, it is important to obtain quantitative information on the temperature dependence of the behavior of La atoms confined in the B cages.

For the observation of local dynamics, the time-differential perturbed angular correlation (TDPAC) method exhibits its remarkable power. The TDPAC method is a spectroscopy using unstable nuclei as the probe. By observing the time-variant directional anisotropy of γ rays successively emitted in the disintegration process of the excited nucleus of the probe, we can obtain direct information on local fields in the vicinity of the probe nucleus through electromagnetic interactions between the probe nucleus and extranuclear field.[4,5] This method is well suited to the present study because the ^{140}Ce probe, the daughter nucleus of ^{140}La produced by the neutron capture reaction of ^{139}La, has a potential to give information on local dynamics as has been reported in our previous works.[6–9] Taking advantage of this spectroscopy, we have succeeded in observing dynamic motion of the probe atoms. Showing temperature-dependent fluctuation of the extranuclear field, in this Brief Report, the local mobility of the probe atoms is discussed based on the time scale and temperature dependence of their rattling motion.

II. EXPERIMENT

Lanthanum hexaboride powder of about 54 mg was heat-sealed in a polyethylene tube. For the production of TDPAC probes by the ^{139}La$(n,\gamma)^{140}$La reaction, neutron irradiation was performed for the sealed sample in a pneumatic tube at the research reactor of Kyoto University with a thermal neutron flux of 2.75×10^{13} cm^{-2} s^{-1} for 1 min. After the irradiation, TDPAC measurements were performed at various temperatures for the probe ^{140}Ce($\leftarrow^{140}$La) on the 329–487 keV cascade γ rays with the intermediate state of $I^{\pi}=4^{+}$ having a half life of 3.45 ns. (Note that no noticeable change was observed in the TDPAC spectra for the sample annealed at 773 K in vacuum after the neutron irradiation. It is considered that the sample was little damaged because of the short irradiation time). A simplified decay scheme of ^{140}Ce formed in the disintegration process of radioactive ^{140}La is shown in Fig. 2.[10] In the present work, the time evolution of the directional anisotropy was derived by the following simple arithmetic operation:

$$A_{22}G_{22}(t)=\frac{2[N(\pi,t)-N(\pi/2,t)]}{N(\pi,t)+2N(\pi/2,t)}, \quad (1)$$

where A_{22} denotes the angular correlation coefficient representing the magnitude of the directional anisotropy of the cascade γ rays, $G_{22}(t)$ is the time-differential perturbation factor as a function of the time interval, t, between the cas-

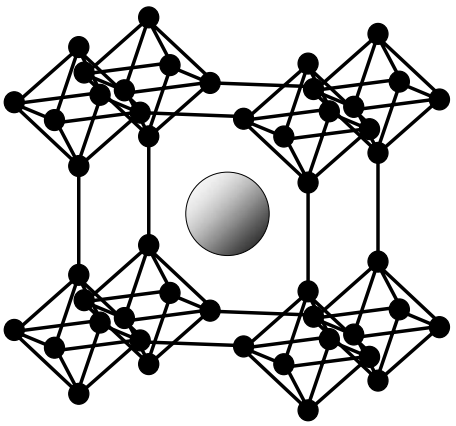

FIG. 1. Crystal structure of LaB_6. The La atom (the large dark circle) is positioned in the three dimensional cage of B atoms (the small black circles).

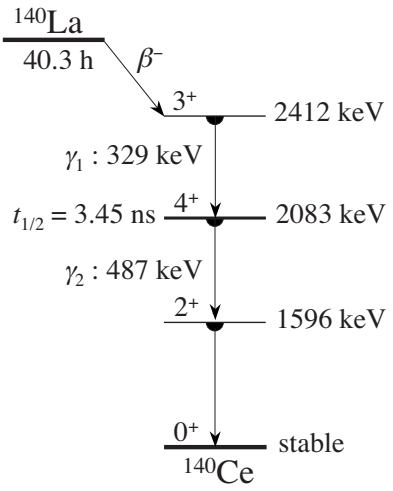

FIG. 2. Simplified decay scheme of ^{140}Ce formed in the disintegration of ^{140}La. For the symbols and numbers, see Ref. 10.

cade γ-ray emissions, and $N(\theta,t)$ is the number of the coincidence events observed at an angle, θ. For the γ-ray detection, BaF_2 scintillation detectors were adopted due to their excellent time resolution.

III. RESULTS AND DISCUSSION

A. Dynamic motion at higher temperatures

The TDPAC spectra of ^{140}Ce transmuted from some La in LaB_6 are shown in Fig. 3. One can obviously see relaxation of the directional anisotropy in each of the spectra. According to the diffusion approximation proposed by Abragam and Pound,[11] the directional anisotropy of a TDPAC spectrum is expected to show exponential-type relaxation when the relevant nuclear spins experience a dynamic perturbation caused by fast fluctuation of the extranuclear field.[12] Following the theoretical description, all the spectra were fitted by assuming a single component with

$$G_{22}(t) = \exp(-\lambda t), \tag{2}$$

where λ represents the relaxation constant. As shown with the solid lines, the fits reproduce all the spectra well except for the one measured at 10 K.

Because the relevant intermediate state of the cascade γ-ray emissions has a nuclear spin of $I=4$ as shown in Fig. 2, the nucleus in the state has an electric quadrupole moment, as well as a magnetic dipole moment, which allows it to have electromagnetic interactions with outer surrounding spins and/or charge distributions. In the present case, therefore, two different mechanisms are considered for the nuclear relaxation: (i) nuclear spin relaxation through $4f$ spin fluctuation and (ii) nuclear quadrupole relaxation caused by the fluctuation of the extranuclear charge distribution. In either case, the chemical state of the probe Ce ion is considered to be trivalent, $^{140}Ce^{3+}$, because the fast relaxation in the present short time window would not take place without a strong perturbation by the large field produced by a $4f$ electron.[6–9] Even in the presence of a $4f$ electron, however, the effective magnetic field in paramagnetic atoms is considered to be zero in general in the absence of an external magnetic field. The former possibility can thus be excluded, and the present dynamic perturbation can be attributed to the relative motion of the probe nucleus to the outer surrounding charge distribution.

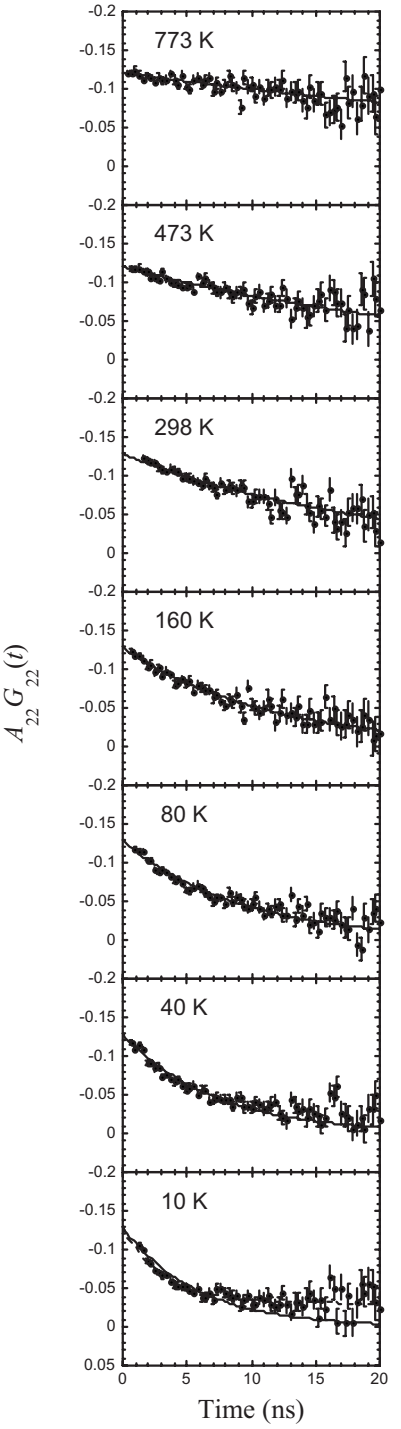

FIG. 3. TDPAC spectra of ^{140}Ce($\leftarrow^{140}$La) confined in the B cage measured at the temperatures indicated. Least-squares fits with Eq. (2) were performed as indicated by the solid lines. The dotted line in the 10 K spectrum is the result of a fit with Eq. (5).

We find from Fig. 3 that the relaxation rate of the directional anisotropy has an apparent temperature dependence. In

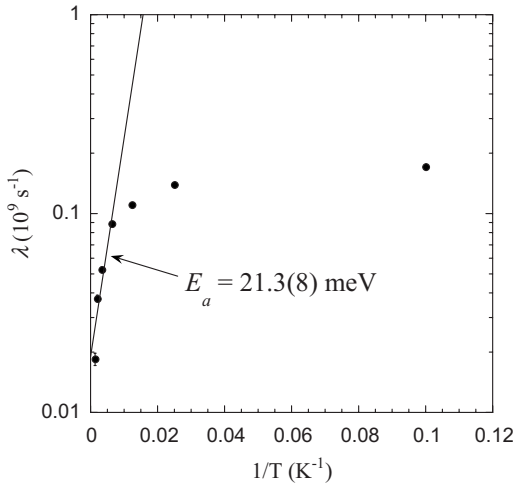

FIG. 4. Temperature dependence of the relaxation constant, λ. The data for the high-temperature range between 160 and 773 K are fitted with an Arrhenius-type equation, Eq. (3), and the deduced value of the activation energy (E_a) is indicated.

order to investigate the trend in detail, the relaxation constant, λ, was plotted as a function of the reciprocal temperature in Fig. 4. The relaxation constant becomes smaller as the temperature rises, which unequivocally suggests that the probe nucleus moves faster at higher temperatures by thermal activation. The activation energy, E_a, of the thermal motion at the high-temperature range between 773 and 160 K was obtained by a least-squares fit to the λ values with the following Arrhenius-type equation:

$$\lambda = A \exp\left(\frac{E_a}{k_B T}\right), \tag{3}$$

where A denotes the attempt relaxation rate, which was determined to be $A=1.97(8)\times 10^7$ s^{-1}. The activation energy was estimated to be $E_a=21.3(8)$ meV, which is in the same order as the corresponding values for the rattling motions observed for other clathrate compounds.[13–15] According to an *ab initio* calculation, the migration enthalpy of La in the bulk is $\Delta H_{\mathrm{mig}}=5.9$ eV.[16] Since this value is by far greater than the present E_a, it is difficult to regard the dynamic movement of the probe nucleus as hopping motion among La sites. The observed movement is therefore assigned to the rattling motion of ^{140}Ce in the cage of B atoms. The time scale of the motion can be deduced from the following well-established relation for this probe:[4,6,11]

$$\tau_c = \frac{5}{1314}\frac{\lambda}{\omega_Q^2}. \tag{4}$$

Since the nuclear quadrupole frequency, ω_Q, of the precession of the ^{140}Ce probe nucleus is at most 10^8 rad s^{-1} in the presence of a $4f$ electron,[8] and the relaxation constant, λ, is $5.3(2)\times 10^7$ s^{-1} at room temperature, for example, the correlation time, τ_c, of the probe for the rattling motion is in the order of 10^{-11}-10^{-10} s. It is accordingly considered that the motion is not a mere atomic vibration, whose frequency would be in the order of 10^{12}–10^{14} s^{-1},[16] but a slower motion with a large amplitude in such a way that the direction of the principal axis of the electric field gradient (EFG) at the probe nucleus changes at the deduced time scale.

B. Motional freezing of the rattling at low temperature

At lower temperatures, the data points in Fig. 4 deviate from the fitted line with Eq. (3). This trend can be interpreted as signifying a transitive state where the rattling motion of the probe atoms is slowing down to freezing in the present time scale due to lack of thermal energy. The freezing phenomenon of the rattling is seen most evidently in the spectrum measured at 10 K; the directional anisotropy does not seem to reach zero asymptotically, and the least-squares fit with Eq. (2) consequently fails. If all the probe atoms reside in a specific lattice site, most probably in the center of the B cage, at such a low temperature that the slow rattling would freeze, static perturbation should be observed through electric quadrupole interactions. The TDPAC spectrum at 10 K is, however, not dominated by oscillations reflecting an expected strong interaction with the large extranuclear field produced by a $4f$ electron. It is therefore considered from this observation that another dynamic effect that interferes with nuclear precession is operative and becomes observable in the spectrum at this low temperature.[17] The angular correlation remains unperturbed under the condition that the frequency of the extranuclear fluctuation is too fast to cause nuclear spin relaxation, which is the extreme of the condition accounted for in Ref. 12. Assuming this situation, a least-squares fit was performed with the following equation including the unperturbed component by a first approximation:

$$G_{22}^{*}(t) = f \exp(-\lambda t) + (1-f), \tag{5}$$

where f stands for the fraction of the exponentially attenuating component, which was estimated to be 76(2)% at this temperature. The fit is satisfactory as indicated by the dotted line in the 10 K spectrum in Fig. 3.

It is evident from Eq. (4) that the directional anisotropy is little attenuated in the present observation time if $\tau_c < 10^{-12}$ s. In LaB_6, one electron is effectively promoted into the conduction band per unit cell, leading to metallic conductivity. As has been reported for other hexaboride compounds,[18] accordingly, lattice vibration of a frequency of $\geq 10^{12}$ s^{-1} through the electron-phonon interaction may be a cause of such fast fluctuation of the extranuclear field at the low temperature.

IV. SUMMARY AND CONCLUSIONS

In the present work, slow rattling motion of the probe ^{140}Ce as the β^- decay product of ^{140}La confined in the B cage of LaB_6 was observed at a time scale of 10^{-11}-10^{-10} s by means of the TDPAC method. From the temperature-dependent relaxation constant values, λ, for the directional anisotropy of the cascade γ rays, the activation energy of the motion at higher temperatures (160 to 773 K) was deduced to be $E_a=21.3(8)$ meV. At lower temperatures down to 10 K, the λ values deviate from the constant trend of the tem-

perature dependence, signifying a transitive state to motional freezing at this time scale. However, the rattling motion is still active for 76(2)% of the probes at temperature as low as 10 K. The other component of 24% seems to be unperturbed at this low temperature. A possible interpretation was given to this observation: another dynamic mode—lattice vibration through the electron-phonon interaction—became observable at the low temperature because of the freezing of the slow rattling with a large amplitude. In this work, we were able to obtain quantitative information on the dynamic motion of the metal atoms confined in the B cages. The present microscopic observation would be a help for the investigation of intriguing low-temperature physics of hexaboride compounds.

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[1] Y. Peysson, B. Daudin, M. Dubus, and R. E. Benenson, Phys. Rev. B **34**, 8367 (1986).
[2] D. Mandrus, B. C. Sales, and R. Jin, Phys. Rev. B **64**, 012302 (2001).
[3] M. Kohgi, K. Kuwahara, N. Ogita, M. Udagawa, and F. Iga, J. Phys. Soc. Jpn. **75**, 085003 (2006).
[4] H. Frauenfelder and R. M. Steffen, in *α-, β-, and γ-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland, Amsterdam, 1965), Vol. 2, p. 997.
[5] G. Schatz and A. Weidinger, *Nuclear Condensed Matter Physics* (Wiley, New York, 1996).
[6] W. Sato, K. Sueki, K. Kikuchi, K. Kobayashi, S. Suzuki, Y. Achiba, H. Nakahara, Y. Ohkubo, F. Ambe, and K. Asai, Phys. Rev. Lett. **80**, 133 (1998).
[7] W. Sato, K. Sueki, K. Kikuchi, S. Suzuki, Y. Achiba, H. Nakahara, Y. Ohkubo, K. Asai, and F. Ambe, Phys. Rev. B **58**, 10850 (1998).
[8] W. Sato, K. Sueki, Y. Achiba, H. Nakahara, Y. Ohkubo, and K. Asai, Phys. Rev. B **63**, 024405 (2001).
[9] W. Sato, H. Ueno, A. Taniguchi, Y. Itsuki, Y. Kasamatsu, A. Shinohara, K. Asahi, K. Asai, and Y. Ohkubo, Phys. Rev. B **74**, 214302 (2006).
[10] *Table of Isotopes*, 8th ed., edited by R. B. Firestone and V. S. Shirley (Wiley, New York, 1996), Vol. 1.
[11] A. Abragam and R. V. Pound, Phys. Rev. **92**, 943 (1953).
[12] This theory is applied to the situation that the reciprocal frequency of nuclear precession caused by a static electromagnetic perturbation from the extranuclear field is much greater than the correlation time for the reorientation of the perturbing field.
[13] Y. Nemoto, T. Yamaguchi, T. Horino, M. Akatsu, T. Yanagisawa, T. Goto, O. Suzuki, A. Dönni, and T. Komatsubara, Phys. Rev. B **68**, 184109 (2003).
[14] T. Goto, Y. Nemoto, K. Sakai, T. Yamaguchi, M. Akatsu, T. Yanagisawa, H. Hazama, K. Onuki, H. Sugawara, and H. Sato, Phys. Rev. B **69**, 180511(R) (2004).
[15] T. Goto, Y. Nemoto, T. Yamaguchi, M. Akatsu, T. Yanagisawa, O. Suzuki, and H. Kitazawa, Phys. Rev. B **70**, 184126 (2004).
[16] R. Monnier and B. Delley, Phys. Rev. B **70**, 193403 (2004).
[17] There is another candidate for the interpretation of the remaining anisotropic component at longer times: the presence of multiple components having electrostatic interactions with different EFGs. We thus attempted to reproduce the data by fits assuming such components with widely ranged EFGs. Because the attempt was not successful, however, this possibility was excluded.
[18] N. Ogita, S. Nagai, N. Okamoto, M. Udagawa, F. Iga, M. Sera, J. Akimitsu, and S. Kunii, Phys. Rev. B **68**, 224305 (2003).