The First Determination of Spin–Lattice Relaxation Times (T_1) of ^{73}Ge in the Solid State

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Spin–lattice relaxation times (T_1) of ^{73}Ge nuclei of tetraphenylgermane (**1**) and some other organogermanes in solid state and metallic germanium were determined under the high-resolution condition. T_1 values were found in the order of s in agreement with the reported value for metallic germanium determined in the static condition.

It has generally been taken for granted that observation of ^{73}Ge resonance in the solid state is extremely difficult or even impossible because of its low natural abundance (7.8 %), small nuclear magnetic moment ($\mu/\mu_N = -0.87677$) and large nuclear spin (I = -9/2). In the previous communication, however, we reported high-resolution solid-state MAS (magic angle spinning) ^{73}Ge NMR spectra of tetraphenylgermane (**1**) and tetrabenzylgermane (**2**).[1] To the best of our knowledge, this is the first observation of ^{73}Ge signals of organogermanium compounds in the solid state.

We initially assumed that the determination of spin–lattice relaxation times (T_1) of ^{73}Ge nuclei in the solid state is even more difficult since ^{73}Ge signals in the solid state should be very broad and hence T_1 is very short. This is indeed the reason why no one has attempted to measure ^{73}Ge resonance (T_1 as well as chemical shifts) in the solid state before we attempted.

Our finding that **1** exhibited a reasonably narrow signal (half-width; 40 Hz) in the solid state prompted us to determine its T_1. Initially we assumed that the T_1 value in the solid state is, at the longest, in the same order as that in solution, that is, in the order of ms. We soon found that this assumption was not correct since the use of short pulse delay (e.g., 50 ms) matching to a short T_1 gave poor results. The signal was, however, properly accumulated when a longer delay was used (e.g. 25 s), which indicates that T_1 is in the order of s. Indeed, we could determine T_1 of **1** with inversion–recovery method. The measured T_1 of **1** is 2.6 s, which makes a sharp contrast with T_1 of the same compound in solution (0.42 s).[2]

Since it is rather hopeless to determine T_1 of **2** which has a large half-width (350 Hz), we prepared some other symmetrically substituted tetraarylgermanes, (p-$C_6H_5C_6H_4)_4$Ge (**3**) and (p-$MeC_6H_4)_4$Ge (**4**). The half-width of **3** is 78 Hz while that of **4** is as large as 390 Hz. It was possible to determine T_1 of **3** (ca. 1.2 s) though the error might be proportionally large. T_1 values for **2** and **4** could not be obtained accurately, but we can safely guess, from the null-points of inversion–recovery stack plots, these are in the order of 0.1 s (e.g., ca. 0.6 s for **4**).

Now we can conclude that T_1 values of symmetrically substituted germanes are in the order of s, and that the value decreases to the order of 0.1 s as the half-width of the signal increases. This is in a good contrast with the T_1 values of other group 14 element compounds in solid state. Thus, the ^{29}Si T_1 value of naklite is reported to be as long as ca. 1.3 h.[3] This seems to indicate that as far as relaxation study of solid sample is concerned, ^{73}Ge NMR is more practical than ^{29}Si NMR.

Our T_1 value is in agreement with the relaxation times of ^{73}Ge nuclei of germanium single crystals (**5**) at different isotopic content by Vakubovski et al.[4] In order to examine the influence of isotopic disorder on the local deformations in a single crystals, they determined the T_1 by means of saturation recovery method at the static condition. They reported that at ambient temperature, the T_1 values are in the range of 11–12.4 s and the isotopic distribution does not make much change.

Since the measurement of T_1 of **5** by Russian investigators was carried out without MAS, we repeated the measurement of powdered germanium (**6**; natural isotopic abundance sample) with and without MAS by inversion–recovery method. A typical stacked plot is given in Figure 1. The T_1 value we obtained is 10.6 s, which is essentially identical with the reported value.

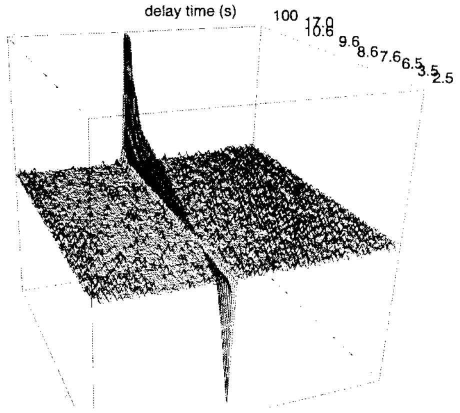

Figure 1. ^{73}Ge inversion–recovery spectra of **6.**

At the natural abundance level, the half-width of **5** was ca. 40–80 Hz.[4] Our measurement without MAS also gives the value of 60 Hz, but with MAS the signal is substantially sharpened, and the half-width is 18 Hz, which indicated that the MAS does affect on the half-width to a considerable extent. Since there is little, if any, dipolar interaction among germanium nuclei in solid state, MAS seems to reduce the broadening due to the quadrupolar interaction to some extent.

One interesting aspect as for the half-width is the value for isotopically enriched germanium. We determined the half-width and T_1 of ^{73}Ge (>98 at. wt %).[5] Though there is no change in T_1, the half-width is increased to 230 Hz (Figure 2). This can be explained in terms of the homonuclear dipolar interaction[6] among the same isotopes which makes difficult the measurement of solid state NMR for some abundant nuclei.

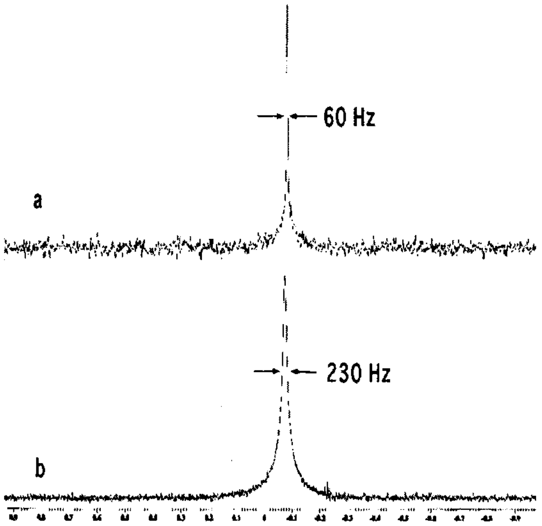

Figure 2. Half-width of natural abundance and enriched ^{73}Ge metal. a) natural abundance sample **6**. b) ^{73}Ge enriched sample.

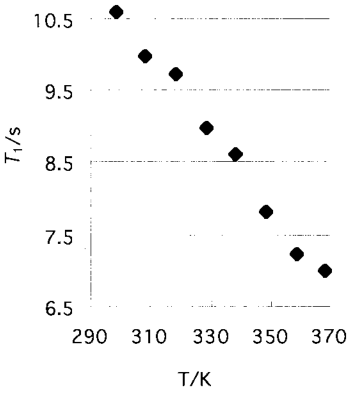

Figure 3. Temperature dependence of T_1 of **6**.

Since ^{73}Ge is a quadrupolar nucleus, the spin–lattice relaxation would most likely proceed via quadrupolar mechanism. We determined T_1 of **6** at the temperature ranging from 290 K to 370 K. Though the range is narrow, the temperature dependence of T_1 is clear; there is a negative dependence, i. e., as the temperature increases, T_1 linearly decreases (Figure 3). The Russian investigators also determined the temperature dependence of T_1 of **5** at lower temperature; at 300 K, T_1 is ca. 12 s while at 50 K it is as long as 1300 s, and based on this, the concluded that the relaxation proceeds via quadrupolar mechanism.

We believe that in the case of organogermanium compounds, the relaxation mechanism in the solid state is the same with that in solution where the quadrupolar mechanism was proved predominant.[7] We could confirm the absence of dipolar mechanism by determining that the NOE enhancement factor is zero for **1**.

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References and Note

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2 The ^{73}Ge NMR spectra were recorded with JEOL ECP 300 spectrometer operating at 10.48 MHz, equipped with a probe modified for this purpose. The design of the probe is essentially the same with one for observation of ^{107}Ag. To obtain the best matching, a dummy condenser was attached in series. The cross polarization was not applied. Typically, 208 mg of **1** was packed in a 7-mm (o. d.) cell, which was rotated at 4800 Hz. For inversion recovery measurement, the following conditions were used; pulse delay, 25 s; number of accumulation, 100 for **1**; sweep width, 5 kHz. The waiting time was changed from 0.05s to 10 s at 0.1 s interval.

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5 Purchased from CK Gas Products Ltd, UK.

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