NMR study of slow atomic motion in Sr$_8$Ga$_{16}$Ge$_{30}$ clathrate

Weiping Gou, Yang Li, Ji Chi, and Joseph H. Ross, Jr.
Department of Physics, Texas A&M University, College Station, Texas 77843-4242, USA

M. Beekman and G. S. Nolas
Department of Physics, University of South Florida, Tampa, Florida 33620-5700, USA

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The clathrates feature large cages of silicon, germanium, or tin, with guest atoms in the cage centers. Sr$_8$Ga$_{16}$Ge$_{30}$ clathrate is interesting because of its thermoelectric efficiency, and its glasslike thermal conductivity at low temperatures, indicating Sr atom hopping within the cages. We measured $^{71}$Ga NMR with a 9 T superconducting spectrometer down to 1.9 K. Knight shift and $T_1$ results are consistent with low density metallic behavior. The lineshapes exhibit changes consistent with motional narrowing at low temperatures, and this indicates unusually slow hopping rates. Fitting these line shape changes yielded an activation energy of about 7 K. To further investigate this behavior, we made a series of measurements using the Carr-Purcell-Meiboom-Gill NMR sequence. Fitting the results to a hopping model yielded an activation energy of 4.6 K, consistent with the line shape result. We can understand all of our observations in terms of nonresonant atomic tunneling between asymmetric sites within the cages, in the presence of disorder.

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I. INTRODUCTION

Clathrates consist of cages of silicon, germanium, or tin in a crystalline framework, with guest atoms located inside the cages. Recently these materials have attracted considerable attention due to their thermal and thermoelectric properties. The type-I clathrates Sr$_8$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ga$_{16}$Ge$_{30}$ have been observed to have glasslike thermal conductivity at low temperatures, while Ba$_8$Ga$_{16}$Ge$_{30}$ does not behave this way. Structural studies performed on Sr$_8$Ga$_{16}$Ge$_{30}$, Ba$_8$Ga$_{16}$Ge$_{30}$, and Eu$_8$Ga$_{16}$Ge$_{30}$ include single-crystal neutron-diffraction measurements, which showed that Sr and Eu atoms in the larger cages of the type-I structure have a small displacement off the center position to one of four crystallographically equivalent positions at low temperatures, while Ba atoms remain at the center. This provides a connection between the thermal response and atomic displacements within the cages. Recent low temperature ultrasonic attenuation measurements on a Sr$_8$Ga$_{16}$Ge$_{30}$ single crystal provided additional evidence for a relatively high concentration of tunneling states, a feature normally associated with bulk tunneling states, a feature normally associated with bulk tunneling states was described for the Eu clathrate. However the specific model for the tunnel barriers between four-well tunneling states in this material.

II. EXPERIMENTAL METHODS

Sr$_8$Ga$_{16}$Ge$_{30}$ crystals were prepared as follows. Stoichiometric quantities of the high-purity constituent elements were mixed and reacted in pyrolic boron nitride (BN) crucibles for 24 h at 950 °C then annealed at 700 °C for 24 h. The BN crucibles were themselves sealed inside a fused quartz ampoule, which was evacuated and backfilled with nitrogen gas to a pressure of two-thirds of an atmosphere. The ingots were composed of crystallites with dimensions of one to three cubic millimeters. The ingots are stable in air and water but were etched with aqua regia for metallographic analysis, which indicated single-phase material. X-ray diffraction measurements were used for further characterization, which verified the crystallinity and phase purity of the specimen.

NMR experiments were performed at a fixed field of 9 T using a homebuilt pulse spectrometer. The field was calibrated using a Ga(NO$_3$)$_3$ dilute solution as $^{71}$Ga zero-shift reference (frequency close to 115 MHz). The sample for NMR measurements was several cubic millimeters, made into powder, and mixed with KBr.

III. MEASUREMENTS AND DISCUSSION

NMR spectra of Sr$_8$Ga$_{16}$Ge$_{30}$ at room temperature and 4.2 K are shown in Fig. 1, measured by echo integration. A room-temperature search over a considerably wider range of relaxation times, obscuring the hopping behavior in that case, however below we show that for the Sr clathrate, pulsed NMR techniques can resolve the relatively slow Sr hopping behavior at low temperatures. In addition, we describe Knight shift and $T_1$ relaxation results which provide a measure of the low-density conduction electron concentration in this material.
FIG. 1. Line shapes at room temperature and 4.2 K, offset vertically for clarity.

shifts verified this broadened line to be the only observable signal. Since it is known\textsuperscript{10} that Ga occupies all three crystallographic sites in Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}, the single NMR line observed at both temperatures is presumably due to a superposition of signals from these three sites, with their individual powder patterns.

Measured signals correspond to the central transition ($-1/2 \leftrightarrow 1/2$) for \textit{I}=3/2 \textsuperscript{71}Ga, which was confirmed by comparing the pulse length for the Ga(NO\textsubscript{3})\textsubscript{3} solution with those of the Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} sample.\textsuperscript{11} This situation is not uncommon in alloy samples, for which random quadrupole couplings can leave the satellite transitions broadened into a featureless background, with the relatively narrow central transition affected only to second order in the quadrupole coupling. \textit{T}\textsubscript{1} measurements at the center of the line shape were done by use of the sequence 180\textdegree-(\textit{T}\textsubscript{wait})-90\textdegree-(\tau)-180\textdegree--(\tau)-echo. The data were fitted to a multiexponential relaxation curve assuming magnetic relaxation for the central transition to obtain \textit{T}\textsubscript{1}.\textsuperscript{12} The data agreed well with these curves over the whole temperature range. The \textit{T}\textsubscript{1} results are shown in Fig. 2. These data obey the Korringa relation, a signature of metallic behavior,\textsuperscript{13} with \textit{T}\textsubscript{1}T = 8.5 sK obtained by least squares fitting. The Knight shift of the center of mass of the line shape is almost independent of temperature around \textit{K}=0.084\% (Fig. 2 inset). These results indicate that \textit{T}\textsubscript{1} and \textit{K} are dominated by interactions with conduction electrons, and that Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} is doped into the metallic regime. This is in agreement with electrical transport for this material,\textsuperscript{2,4,14} which typically indicates \textit{n}-type behavior, and carrier densities in the range 10\textsuperscript{20} to 10\textsuperscript{21} cm\textsuperscript{-3}, due apparently to intrinsic defects.

Combining the observed \textit{T}\textsubscript{1} and \textit{K} to form the Korringa product yields \textit{K}\textsuperscript{2}\textit{T}\textsubscript{1} = 5.9 \times 10\textsuperscript{-6} sK. The free-electron value for \textsuperscript{71}Ga is 2.73 \times 10\textsuperscript{-6} sK, obtained from\textsuperscript{13}

\begin{equation}
\textit{K}^2\textit{T}_1 = \frac{\hbar}{4\pi\gamma_e^2\gamma_n^2},
\end{equation}

where \(\gamma_e\) is the gyromagnetic ratio of the electron, \(\gamma_n\) is the gyromagnetic ratio of the nucleus, and \(\kappa\) is the Boltzmann constant. The observed Korringa product is enhanced by a factor of approximately 2.2, which is typical of ordinary metals, and indicative of normal metallic behavior. By contrast the Korringa product in disordered systems containing localized electrons will be strongly enhanced,\textsuperscript{15,16} a signature of the effects of the strong correlations.\textsuperscript{17,18} Note that in Na\textsubscript{3}Ba\textsubscript{3}Si\textsubscript{6} clathrate, a similar modest Korringa enhancement has been observed.\textsuperscript{19} However, in that case, \(\textit{K}\) is temperature dependent, indicating possible sharp features in the electronic structure,\textsuperscript{20} for which there is no evidence in the present case.

For further analysis, we used a parabolic band approximation to estimate \(\textit{K}\). We assume a spherical Fermi surface, with a conduction band \textit{s}-orbital fraction equal to 1/4 (corresponding to \textit{sp}\textsuperscript{3} hybridization) \(m^* = 3m_e\) and \(n=1.5 \times 10\textsuperscript{20} \text{cm}^{-3}\), which are typical values for samples of this material,\textsuperscript{14} and the hyperfine field for Ga, \(H_{HF} = 620\text{ T}.\textsuperscript{21}\) These values yield \(\textit{K}=0.2\%\), which is slightly larger than observed. Thus, the relatively small \(\textit{K}\) is consistent with the accepted electrical properties of Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}. Note that the quantity which we identify as \(\textit{K}\) is actually an average of individual \(\textit{K}\) values from among the three crystallographically inequivalent framework sites, because of the overlapping of lines. NMR lines for these sites can be seen individually in \textsuperscript{29}Si NMR (Ref. 19) or possibly partially separated by magic angle spinning in Ga NMR.\textsuperscript{22}

The second-order quadrupole coupling can give further line shifts for the central transition, as well as broadening the line. To analyze for this effect, we performed \textsuperscript{69}Ga NMR measurements at room temperature. We found that the center shift is 0.085\% for \textsuperscript{69}Ga, compared to 0.084\% for \textsuperscript{71}Ga. \textsuperscript{69}Ga has a quadrupole moment \(Q=0.178 \times 10\textsuperscript{-28} \text{m}^2\), compared to 0.112 \times 10\textsuperscript{-28} \text{m}^2 for \textsuperscript{71}Ga, and the second-order quadrupole shift is proportional to \(Q\textsuperscript{2}.\textsuperscript{13}\) The small observed difference is comparable to the experimental error, and indicates that the second-order quadrupole contribution to this shift is very small. This justifies the approximation used above, in which the center shift was interpreted as a Knight shift, of magnetic origin. Furthermore, we found that the linewidth for \textsuperscript{69}Ga exceeds that of \textsuperscript{71}Ga, with a ratio of the full widths at half maximum equal to 2.34, which is slightly smaller than the ratio, \((Q(\textsuperscript{69}Ga)/Q(\textsuperscript{71}Ga)^2 = 2.53\), expected for broadening due en-
Fitting this expression to the high-T \( T \) case of an activated process, where \( E_a \) is large, and the decay curve is exponential, which indicates that the echo decay is dominated by motion. However at high \( T \), \( \alpha \) is small, indicating that the motional contribution is averaged out, leaving a Gaussian decay due to like-spin coupling.\(^{23} \) At high \( T \), fast motion will cause more of the spin-spin coupling to be like-spin in character, which makes the linewidth shorter. This is consistent with the observed behavior, and thus the picture established above, whereby the NMR line is subject to progressive motional narrowing as the temperature is raised, agrees with the spin-echo decay results.

In order to further understand the motion process, we performed measurements using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. The sequence is 90°-\((\tau)\)-180°-\((\tau)\)-echo-(\(\tau\))\(^4\). where \( \tau \) is half of the spacing between 180° pulses. The results at RT, 77 K, 32 K, and 4.2 K are shown by Fig. 5. We can see that as \( \tau \) increases, the echo decay rate becomes smaller, at all temperatures. One common mechanism for this type of decay in a CPMG experiment is diffusion of the atoms under observation. However, since the Ga atoms are bonded to the framework, low-temperature Ga motions, however, can slowly modulate the Ga-site quadrupole shifts, providing a decay similar to what we observed. We cannot tell solely from these results whether Sr atoms are hopping between cages or between sites within the same cage, however since the energy barrier is evidently quite small, we will assume that these dynamics are associated with the rattling-type motion of Sr within the type-I clathrate cages.\(^2 \)

For random hopping, the linewidth can be related to a correlation time, which will follow \( \tau_c = \tau_o \exp(\gamma / kT) \) in the case of an activated process, where \( \gamma \) is the activation energy of the system. Motions of atoms in the near vicinity of the Ga nuclei being observed will cause changes in the electric field gradient, and thus shifts in the NMR resonance position, due to the electric quadrupole effect. Because of the superposition of many orientations, we can see only a broadening, rather than a splitting or shift. In the motionally narrowed limit, the linewidth is proportional to \( \tau_c \), so that the linewidth can be fitted to \( W_c = W_o \exp(\gamma / kT) \) to find \( \gamma \). Fitting this expression to the high-\( T \) tail we find that \( \gamma = 7.2 \) K. This fitted curve is shown in Fig. 3.

As a further measure of the dynamics, the spin-echo decay was measured by use of the standard Hahn spin echo sequence. The results are shown by Fig. 4. The data were fitted by

\[
S = A\{\alpha \exp(-t/T_{2e}) + \exp[-(t/T_{2g})^2]\}.
\]

Generally, an exponential decay is observed where motion is important, while Gaussian decay is characteristic of the static NMR line, dominated by the nuclear dipole-dipole or pseudodipolar couplings.\(^{23} \) Thus the ratio \( \alpha \) is a measure of the relative importance of motion.

The fitting results are shown in Table I. At low \( T \), \( \alpha \) is large, and the decay curve is exponential, which indicates that the echo decay is dominated by motion. However at high \( T \), \( \alpha \) is small, indicating that the motional contribution is averaged out, leaving a Gaussian decay due to like-spin coupling.\(^{23} \) At high \( T \), fast motion will cause more of the spin-spin coupling to be like-spin in character, which makes the linewidth shorter. This is consistent with the observed behavior, and thus the picture established above, whereby the NMR line is subject to progressive motional narrowing as the temperature is raised, agrees with the spin-echo decay results.

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![FIG. 3. 71Ga NMR linewidth (square root of second moment) versus temperature, with activated fit described in text.](image)

![FIG. 4. Spin echo decay rate at different temperatures, with fits described in text.](image)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( T_{2e} ) (ms)</th>
<th>( T_{2g} ) (ms)</th>
<th>( \alpha )</th>
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<tbody>
<tr>
<td>1.9</td>
<td>8.1±1.5</td>
<td>7.7±3.6</td>
<td>5.0±2.8</td>
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<td>2.2</td>
<td>5.6±0.1</td>
<td>7.7±0.1</td>
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<td>4.2</td>
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<td>1.3±0.4</td>
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<td>32</td>
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<td>0.8±0.2</td>
</tr>
<tr>
<td>77</td>
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<tr>
<td>296</td>
<td>2.3±0.6</td>
<td>2.2±0.1</td>
<td>0.3±0.1</td>
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</table>
large cage, as has been discussed previously.\textsuperscript{2-4}

To interpret the data, we have invoked a simplified model in which Sr atoms jump randomly between two positions, making nearby Ga nuclei change resonant frequencies by a difference $D_n$. $D_n$ will have a range of values according to Ga position and crystal orientation. During the calculation we made several assumptions: (1) the motion is very slow, so that normally only one jump occurs between 180° pulses; (2) $\Delta \nu$ has an exponential distribution of the form $P(D_n) = \exp(-D_n/\nu_1)/\nu_1$; and (3) $4\pi^2\nu_1 \gg 1$, where $\tau_c$ is the correlation time. Based on these assumptions, we find that the spin echo amplitude can be expressed as

$$S = A \exp\left(-\frac{t}{T_2}\right)\exp\left(-\frac{t}{\tau_c}\right)\left[1 + \frac{\arctan(2\pi\nu_1 t)}{\pi\nu_1\tau_1}\right]^{1/2\tau_c},$$

where $T_2$ is the spin-spin relaxation time. In the CPMG experiments, the motion-free decay rate $[1/T_2$ in Eq. (3)] in fact differs from the normal spin-spin $T_2$, since spin locking leads to a lengthened decay time close to $T_1$ (it is essentially $T_{1p}$ (Ref. 13)). Spin-locking can be eliminated by the use of a phase-alternating pulse sequence (PAPS),\textsuperscript{24} however measurements using a PAPS in our case yielded ill-formed echoes, due to the superposition of stimulated echoes.\textsuperscript{25} Stimulated echoes can be minimized by a perfectly set 180° pulse, however the large linewidth makes this difficult in the present case. Therefore, we used the standard CPMG sequence, making the spin-locking $T_2$ an adjustable variable.

We found that RT data did not fit Eq. (3) very well, presumably because the high-temperature $T_1$ is too short to develop complete spin locking. Therefore we fit the data for the other three temperatures to Eq. (3). The fitting results are shown in Table II. The results show that the typical Ga Larmor frequency difference $\nu_1$, which may vary due to the Ga atom’s distance from and orientation relative to the moving Sr, is 0.15 kHz. We also fitted the resulting correlation times to the activation energy formula $\tau_c = \tau_{c0}\exp(E_a/kT)$. Figure 6 is the result for this fit, which yields an activation energy $E_a = 4.6$ K. This value is close to the $E_a$ obtained from linewidth measurements.

We have made NMR measurements on several samples of Ba$_8$Ga$_{16}$Ge$_{30}$, which is the structural analog of Sr$_8$Ga$_{16}$Ge$_{30}$, however we find that variability of the Ba clathrate electronic properties obscures the effect being examined in this paper. Ba$_8$Ga$_{16}$Ge$_{30}$ is electrically very similar to Sr$_8$Ga$_{16}$Ge$_{30}$, but diffraction measurements indicate that the Ba atoms remain

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$T_2$ (ms)</th>
<th>$\tau_c$ (ms)</th>
<th>$\nu_1$(kHz)</th>
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<tr>
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</tr>
<tr>
<td>77</td>
<td>18</td>
<td>3.2</td>
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</tr>
</tbody>
</table>

FIG. 5. CPMG measurements at different temperatures. Solid curves for 4.2, 32, and 77 K are fits described in text.

FIG. 6. Correlation time versus temperature. (Solid line is the fitting result according to activation energy formula.)
at the cage centers, in contrast to the Sr behavior. (Note, however, that a recent report\textsuperscript{26} indicates that \textit{p}-type Ba clathrate may share the amorphouslike thermal conductivity.) For all samples we have studied, Ga NMR in Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} exhibits a larger linewidth than in Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}, and the \(T_1\) deviates from a Korringa relation at low temperatures, in contrast to the simple-metallic behavior seen in Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}. There is also a small temperature dependence to the center shift of the Ba-clathrate resonance, not seen in the Sr clathrate. These results are consistent with a tendency toward carrier freezout in the Ba clathrate, and the development of a dilute set of magnetic moments due to these localized carriers, or possibly the presence of narrow features in the electronic density of states, such as exhibited in Na\textsubscript{3}Ga\textsubscript{16}Ge\textsubscript{30}.

There is also a small temperature dependence to the center of the cage at low temperature decrease because of different Ga Lamor frequencies for Sr at different sites.\textsuperscript{13} Considering a general situation of an asymmetric double well potential with two low-lying states differing by energy \(\Delta\), and a potential barrier between them with a tunneling rate \(\Delta_0/\hbar\), it can be shown\textsuperscript{29} that the energy splitting between the two eigenstates is

\[ \Delta E = \sqrt{\Delta^2 + \Delta_0^2}. \]  

This is the model often used for two level systems (TLS) in glassy materials. For a symmetric TLS, where \(\Delta = 0\), the energy splitting of the two states will be the exact tunneling energy. In our systems, we observed a barrier of roughly 5 K, in which case the corresponding tunneling frequency will be \(10^{13}\) Hz. Again this is not what we observed in our experiments. However for an asymmetric TLS, where \(\Delta \neq 0\), from the above expression, \(\Delta_0\) can be much smaller than \(\Delta E\), so the tunneling rate can be dramatically reduced. A broad range of asymmetry parameters is found in many glassy systems, and this is the common way to understand the \(T^2\) behavior of the thermal conductivity.

Thus, we can understand our observations in terms of nonresonant atomic tunneling between asymmetric sites within the cages, in the presence of disorder. There are various possibilities for the source of this disorder. For example, it is known that the Ga atoms are distributed on these framework sites.\textsuperscript{10} Furthermore, Sr vacancies or cage-cage interaction might also contribute. It is true that neutron diffraction measurements show four equivalent positions for each Sr atom,\textsuperscript{2} however this is not inconsistent with an asymmetric well, as long as the asymmetry is randomly distributed, since the scattering experiments do not distinguish static from transient disorder.

One thing that this model cannot explain is the linewidth decrease at the lowest temperatures (below 4 K, see Fig. 3). One possible explanation could be that at very low temperatures the displacement of the guest atoms assumes an ordered configuration. A similar result has been found for Si clathrates,\textsuperscript{30} in which cage-centered sodium atoms are observed to dimerize at low temperatures. A configuration of this type could result in a decreasing linewidth due to decreased strain in the lattice.

IV. CONCLUSIONS

In Ga NMR measurements, we observed linewidth changes indicating slow atomic motion in the Sr clathrate. CPMG measurements yielded results that are consistent with the linewidth changes, assuming the mechanism to be hopping of Sr atoms within the cages. By a simple model, we obtained an activation energy \(E_a=4.6\) K for Sr hopping, which is similar to the value obtained from linewidth measurements. This model assumed a wide distribution of hopping rates, and an asymmetric well model worked well to explain the data. The \(T_1\) of Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} obeys a Korringa relation, implying normal metallic behavior for the Sr clathrate, as expected for a heavily doped \textit{n}-type semiconductor.
ACKNOWLEDGMENTS

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