

# $^{109}\text{Ag}$ NMR investigation of atomic motion in the incommensurate and paraelectric phases of proustite ( $\text{Ag}_3\text{AsS}_3$ )

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(Received 14 May 1999)

$^{109}\text{Ag}$  NMR line shape,  $T_1$ , Hahn spin echo, and Carr-Purcell-Meiboom-Gill (CPMG) spin-echo measurements were performed in proustite ( $\text{Ag}_3\text{AsS}_3$ ) between 420 and 47 K in order to understand the role of atomic motions in phase transitions in a system containing an incommensurate phase. These measurements indicate a definite change in the motional characteristics of Ag ions near 240 K. Above 240 K, an  $\text{Ag}^+$  ion executes fast jump motions between its six inequivalent chemically shifted sites. However, below 240 K, these motions are too slow to affect the line shapes. The NMR line shape results are consistent with the existence of a  $3q$  incommensurate phase between 60 and 50 K. Between 180 and 55 K, Hahn and CPMG spin-echo decay measurements suggest that slow motions exist. These motions are attributed (1) in the paraelectric phase (above 60 K) to slow jumping of an  $\text{Ag}^+$  ion between its inequivalent sites with a jump time of the order of the Hahn spin-echo time and (2) in the incommensurate phase (50–60 K) to ultraslow motion of the incommensurate modulation wave. This paper constitutes a report of the effect on the Hahn spin-echo decay due to atoms jumping between sites characterized by different chemical shifts.

## I. INTRODUCTION

Proustite ( $\text{Ag}_3\text{AsS}_3$ ) is a naturally occurring mineral that has attracted considerable attention not only for its technological applications in nonlinear optics and acousto-electronics<sup>1,2</sup> but also for the wide variety of interesting physical phenomena that it exhibits (e.g., superionic conduction, incommensurate and commensurate phases, and a low-temperature ferroelectric transition). The incommensurate ( $I$ ) phase, which exists between 60 K ( $T_I$ ) and 50 K ( $T_c$ ), is particularly interesting because proustite is one of the few known triply modulated (or  $3q$ ) incommensurate systems (i.e., the incommensurate modulation wave is describable by a six-component order parameter<sup>3</sup>).

The room-temperature trigonal structure of proustite consists of an arsenic and three sulfur atoms which form a covalently bonded  $\text{AsS}_3$  pyramid with an arsenic at the top of each pyramid. Such pyramids are joined by shared silver atoms that are ionically bonded to sulfurs on the pyramids. It has been established<sup>4</sup> that there are 12 possible positions for the silver ions in the unit cell with only six being occupied; the presence of the unoccupied sites is believed to be responsible for some of the physical properties of proustite. The Ag-S bonds in proustite are very weak and, above about 230 K, these bonds break and the Ag begins to diffuse. Above 420 K, proustite becomes a superionic conductor, while at lower temperatures (<200 K) the Ag diffusion is no longer observable.<sup>5</sup>

Although the above sequence of phase transitions and Ag diffusion in proustite are reasonably well understood, there is considerable speculation in the literature about the existence of a broad phase transition near 210 K.<sup>6–8</sup> Raman<sup>6</sup> and Brillouin spectra,<sup>8</sup> ionic conductivity,<sup>5</sup> dielectric constant,<sup>9</sup> and ultrasonic<sup>7</sup> studies have observed anomalies around 210 K. However, x-ray,<sup>3</sup> Raman,<sup>10</sup> and NQR studies<sup>11,12</sup> did not detect any signatures of this phase transition.

The usefulness of magnetic resonance investigations (line shape and relaxation time measurements) in elucidating information about molecular dynamics and associated phase-transition phenomena in condensed systems is well known. In particular, structurally incommensurate systems in which the modulation wave characterizes progressive displacements of atoms from their equilibrium positions can be sensitively probed by studying the magnetic resonance spectrum of a quadrupolar nucleus. The NMR spectrum in the high-temperature paraelectric phase is characterized by discrete lines corresponding to different nuclear sites. However, the development of the incommensurate modulation wave creates an effectively infinite unit cell, resulting in considerable broadening in the NMR spectrum. Since the NMR frequency of a particular nucleus is a function of the internal field and hence of the position, it can be expressed as a power series in the modulation wave order parameters (sp., amplitude and phase). From such an expansion of the NMR frequency, the line shape of all the nuclei subject to the modulation wave can be determined.<sup>13</sup> While singly modulated ( $1q$ ) and doubly modulated ( $2q$ ) incommensurate systems, in principle, have infinite singularities at frequencies determined by the expansion parameters, a  $3q$  incommensurate system exhibits a broad, fairly featureless line with a few van Hove-type singularities.<sup>14</sup>

Previously, incommensurate systems have been studied by investigating the magnetic resonance spectrum of a quadrupolar nucleus [either with pure NQR (Ref. 15) or with quadrupole perturbed NMR (Ref. 13)], since the NQR or NMR frequency of a quadrupolar nucleus is very sensitive to changes in the local internal electric-field gradients induced by the incommensurate modulation wave. There are very few magnetic resonance studies of a nonquadrupolar dipolar (i.e., spin 1/2) nucleus which provide information about incommensurate phase transitions, since the variations in the local dipolar fields (due to the incommensurate modulation wave)

are considerably smaller. Incommensurate line broadening due to a spread in the Knight shift has been observed in the NMR spectrum of a dipolar nucleus ( $^{77}\text{Se}$ ) in the charge-density-wave system,  $2\text{H-TaSe}_2$ .<sup>16</sup> Incommensurate line broadening due to a spread in the chemical shift has also been observed in the  $^{109}\text{Ag}$  NMR spectrum of proustite.<sup>17</sup>

NMR has also provided excellent techniques for estimating atomic and molecular diffusion constants.<sup>18</sup> For a dipolar nucleus, one technique involves the measurement of the Hahn spin-echo decay<sup>19</sup> in the presence of a known externally applied magnetic field gradient  $g$ . The Hahn spin echo then decays<sup>18</sup> as

$$M(2\tau) = M_0 \exp[-2\pi/T_2] \exp[-2D\gamma^2 g^2 \tau^3/3], \quad (1)$$

where  $D$  is the diffusion constant,  $\gamma$  is the gyromagnetic ratio,  $\tau$  is the time between the  $\pi/2$  and  $\pi$  pulses in the Hahn spin-echo experiment, and  $T_2$  is the spin-spin relaxation time. Diffusion constants that are orders of magnitude smaller than those obtained from the above magnetic-field gradient techniques have recently been determined in incommensurate systems.<sup>20,21</sup> In these experiments, Hahn spin-echo measurements were performed on a stationary quadrupolar nucleus subject to a fluctuating electric-field gradient (EFG) arising from modulation wave diffusion. In addition to the magnetization decay arising from spin dephasing due to diffusion in the presence of either an MFG or an EFG, there could also be a magnetization decay due to diffusion in the presence of a chemical shift gradient. From knowledge of the spatial variation of the frequency (quantified by the chemical shift), one can then estimate the diffusion constant from a Hahn echo decay measurement.

In order to understand the physical properties of proustite especially with regard to the possible phase transition (around 210 K) and the  $3q$  incommensurate phase, we performed  $^{109}\text{Ag}$  NMR line shape and relaxation time ( $T_1$  and  $T_2$ ) measurements in a single crystal of proustite over the temperature range covering the paraelectric and incommensurate phases. The line shapes,  $T_1$ , and  $T_2$  indicate a definite change in the  $^{109}\text{Ag}$  motional characteristics near 240 K. The Hahn spin-echo decay exhibits features suggestive of a diffusion type motion between 185 and 55 K, which may be an observation of diffusion-induced dephasing due to a fluctuating chemical shift. The line shape measurements also confirm the existence of the incommensurate phase between 60 and 50 K.

## II. EXPERIMENTAL DETAILS

The  $^{109}\text{Ag}$  NMR experiments were performed in a proustite single crystal at a magnetic field of 8.45 T (corresponding to 16.535 MHz). Our reported line shapes were obtained by Fourier transform of the second half of the spin echo. The pulse sequence used both for the line shape and the Hahn decay measurements was a simple  $\pi/2$ - $\tau$ - $\pi$  sequence.  $T_2$  was measured with a standard CPMG pulse sequence.<sup>22</sup>

Since  $^{109}\text{Ag}$  is a spin-1/2 nucleus with a low gyromagnetic ratio  $\gamma$ , it has an extremely long spin-lattice relaxation time  $T_1$  ( $\sim 30$  h at 80 K) which becomes shorter at higher temperatures because of Ag diffusion. Fortunately, the long  $T_1$  of the  $^{109}\text{Ag}$  nuclei can be shortened considerably by properly orienting the crystal such that the  $^{109}\text{Ag}$  NMR level

spacing becomes comparable to the quadrupolar  $^{75}\text{As}$  NMR level spacing; at this orientation, the  $^{109}\text{Ag}$  can cross relax with the quadrupolar nucleus  $^{75}\text{As}$ , which has a very short  $T_1$  (a few ms). However, the resultant  $^{109}\text{Ag}$   $T_1$  is limited by the cross-relaxation time, which is of the order of many minutes. Using this approach, we were able to shorten the effective  $T_1$  of  $^{109}\text{Ag}$  from 30 h at 80 K at a noncross-relaxation angle, to about 20 min at the cross-relaxation angle. All line shapes reported in this paper were obtained at the cross-relaxation angle. At the cross-relaxation angle the crystal was oriented such that the  $Y$  axis was in the  $B_1$  direction and the angle between the  $Z$  and the  $B_0$  directions was  $14.6^\circ$ , where  $Y$  and  $Z$  are two of the principal axes of the electric-field gradient tensor. Independently, we verified that cross relaxation does not influence the line shape. The  $T_1$  values, obtained by the standard saturation recovery sequence, were, of course, performed at a noncross-relaxation angle. Temperature variation was achieved with an Oxford cryogenic system having a temperature stability of  $\pm 0.1$  K. The pulse sequence generation, signal acquisition, and analysis were performed using a TecMag-Aries NMR system.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Temperature variation of the $^{109}\text{Ag}$ NMR line shape

#### 1. Paraelectric phase (above 60 K)

The temperature variation of  $^{109}\text{Ag}$  NMR line shape in the paraelectric phase between 370 and 64 K in proustite is presented in Fig. 1(a). It is immediately evident that the line shape is markedly different above and below 240 K. Below 240 K, a six-peaked line shape is observed, and this structure remains relatively temperature independent down to 60 K. However above 240 K, the line shape changes significantly and almost disappears around 250 K. A single peaked line shape begins to appear above 250 K and this line continues to narrow with increasing temperature.

The six peaked Ag line shape below 230 K is consistent with the crystal structure of proustite.<sup>23</sup> The Ag atoms in proustite reside between the  $\text{AsS}_3$  pyramids. Since there is a small change in orientation between pyramids in consecutive alternating planes and since there are three Ag atoms for each pyramid, our spectrum, in the absence of jumping between inequivalent sites, is characterized by two groups of three Ag lines (symmetrically placed around the high-temperature motionally narrowed line); each group of lines arises from Ag ions within one of the two inequivalent planes.

For a multiline spectrum, atomic jumps between the different inequivalent sites will first cause the multiline spectrum to merge into a featureless broad spectrum such that the line shape almost disappears. This occurs typically when  $\tau_c \delta\omega \sim 1$ , where  $\tau_c$  is the correlation time associated with the jump process and  $\delta\omega$  is the frequency difference between the jump sites. For  $\delta\omega \sim 5$  kHz [from Fig. 1(a)]  $\tau_c$  is estimated to be about 0.2 ms at 240 K (using  $\tau_c \delta\omega \sim 1$ ). The narrowing of the broadline spectrum at higher temperatures (above 240 K) is consistent with ionic conductivity results<sup>5</sup> and is interpreted by us as motional narrowing due to an increasing jump rate of the Ag ions between different sites on the same

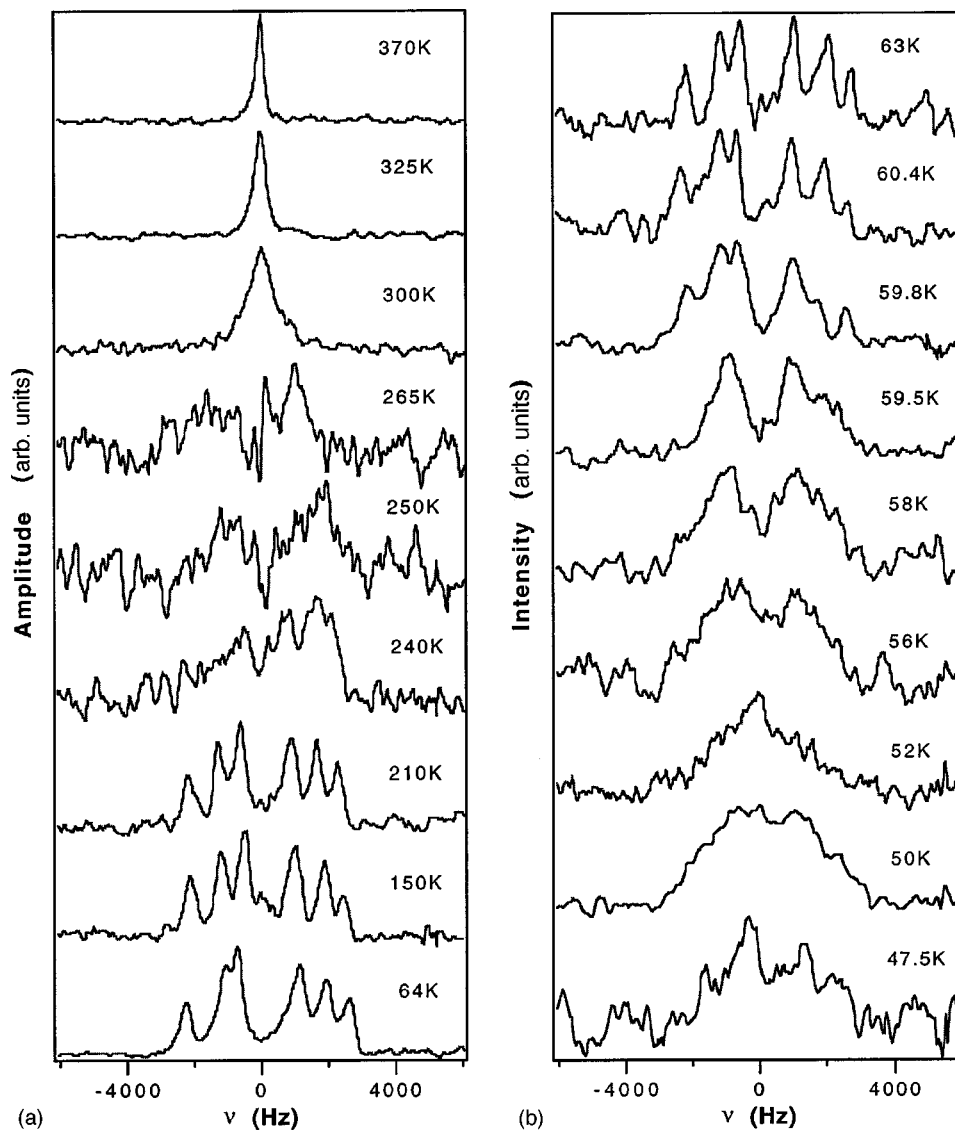


FIG. 1. Temperature variation of  $^{109}\text{Ag}$  NMR line shape in proustite between 370 and 64 K. The central frequency (0 Hz) corresponds to 16.535 MHz. (b) Temperature variation of  $^{109}\text{Ag}$  NMR line shape in proustite between 63 and 47.5 K. The central frequency (0 Hz) corresponds to 16.535 MHz.

$\text{AsS}_3$  pyramids and between sites on neighboring pyramids in different planes.

Our observation of six distinct Ag lines below 240 K suggests that at these lower temperatures the  $\text{Ag}^+$  ions are jumping at a frequency that is slower than the difference in NMR frequency corresponding to the neighboring jump sites (about 500 Hz). The line shape at lower temperatures (below 240 K) remains temperature independent because of the freezing out of the  $\text{Ag}^+$  motions.

The present observations of (i) almost complete disappearance of line shape near 250 K, (ii) a motionally narrowed single line above 270 K, and (iii) appearance of a six-peak structure below 240 K are consistent with a physical picture that  $\text{Ag}^+$  is executing jump motions between its chemically inequivalent sites. The motionally narrowed single line above 240 K suggests rapid jump motions of Ag between all possible sites.

## 2. Incommensurate (50–60 K) and commensurate (below 50 K) phases

The temperature dependence of the line shape in the incommensurate and commensurate phases below 60 K is shown in Fig. 1(b). For comparison, a line shape in the

paraelectric phase (at 63 K) is also included. As the temperature is lowered into the incommensurate phase below  $T_I$  (60 K), the six-peaked spectrum observed above 60 K begins to broaden into two broad peaks symmetrically placed around the position of the high-temperature motionally narrowed NMR line. On further cooling these peaks merge into a much broader single peak. Below  $T_C$  (50 K) additional lines appear on this broad spectrum.

These results clearly show the existence of an incommensurate phase. The broadening of the six peaked structure below 60 K is typical for a phase transition into a structurally incommensurate phase [Fig. 1(b)]. Also the broad and relatively featureless line shape below 60 K is consistent with the predicted spectrum for a  $3q$  incommensurate phase.<sup>14,24</sup> In the upper part of the  $I$  phase (around 58–59 K) the broadening due to the modulation wave is greater than differences in NMR frequency for  $\text{Ag}^+$  ions in the same plane but is not greater than that between Ag ions on different planes; thus we see two featureless broad distributions. As the temperature is lowered further, the amplitude of the incommensurate modulation wave (and, correspondingly, the NMR linewidth) increases, resulting in a merging of this spectrum into a much broader single peaked structure at the lower portion of

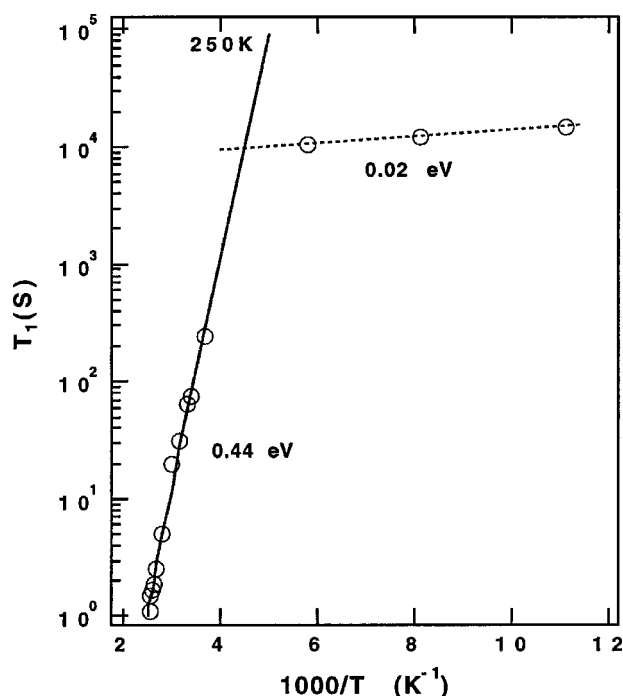


FIG. 2. Temperature variation of the spin-lattice relaxation time  $T_1$  in proustite.

the  $I$  phase (50–52 K). Additional structures in the line shape below 50 K are due to the narrow NMR lines that characterize a commensurate phase.

The NMR linewidth of the  $^{109}\text{Ag}$  is undoubtedly due to spatial variations in the chemical shift of the  $^{109}\text{Ag}$  nucleus. It was earlier observed that the center of the motionally narrowed  $^{109}\text{Ag}$  line (373 K) varies by about 3 kHz as the sample is rotated  $360^\circ$  about the  $Y$  axis, suggesting that the extent of chemical shift anisotropy is of the order of 3 kHz.<sup>17</sup> The incommensurate broadening is then assumed to be due to the spread in chemical shift experienced by the Ag nucleus due to the modulation wave. Our experiments on  $^{109}\text{Ag}$  did not have sufficient signal-to-noise to identify the reported  $1q$  incommensurate phase between 60 and 59.4 K, obtained from  $^{75}\text{As}$  NQR experiments.<sup>24</sup> Furthermore, a spin-1/2 nucleus like  $^{109}\text{Ag}$  (with no quadrupole moment) is much less sensitive to nuclear displacements than is a quadrupolar nucleus like  $^{75}\text{As}$ .

### B. Temperature dependences of the relaxation times $T_1$ and $T_2$

The temperature variations of the spin-lattice ( $T_1$ ) and the spin-spin [Carr-Purcell-Meiboom-Gill (CPMG  $T_2$ )] relaxation times between 420 and 80 K are presented in Figs. 2 and 3, respectively. As with the line shape, two different temperature regions (above and below 240 K) are clearly distinguished.

Above 240 K, both  $T_1$  and  $T_2$  exhibit Arrhenius behavior, with an activation energy for Ag motions of about 0.44 eV, a value which compares well with that obtained from ionic conductivity measurements.<sup>5</sup> This large activation energy suggests that the  $\text{Ag}^+$  mobility rapidly increases with increasing temperature above 240 K. Also,  $T_1$  and  $T_2$  approach each other at 420 K. An extrapolation of the  $T_1$  and  $T_2$  data

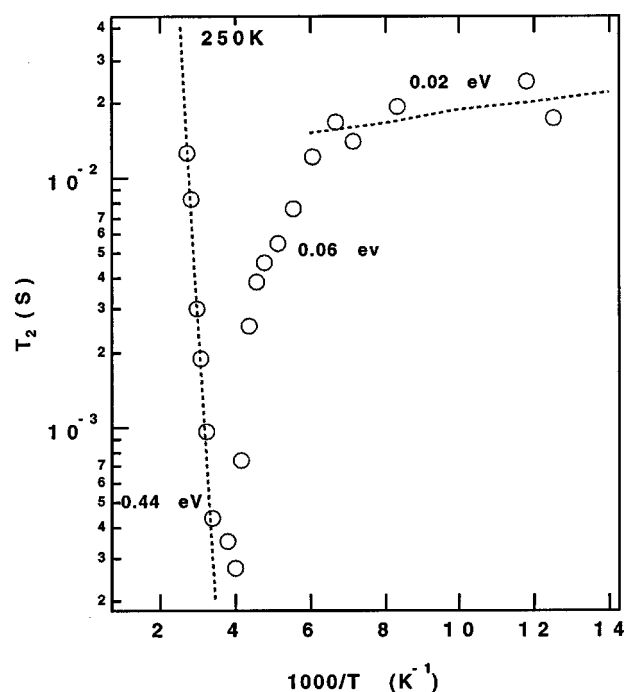


FIG. 3. Temperature variation of the spin-spin relaxation time CPMG  $T_2$  in proustite.

above 240 K suggests that a Bloembergen, Purcell, and Pound<sup>25</sup> (BPP) type  $T_1$  minimum is likely to occur around 420 K, which is consistent with reported observations of superionic behavior in proustite above 420 K.<sup>5</sup> At a BPP minimum,  $\omega_0\tau_c \sim 1$ , where  $\omega_0$  is the Larmor frequency (16.535 MHz for  $^{109}\text{Ag}$  at 8.45 T) and  $\tau_c$  is the correlation time associated with the motional mechanism. Knowing the BPP minimum, the temperature variation of the correlation time between 420 and 230 K can be determined from

$$\tau_c = \tau_0 \exp(-E_a/kT). \quad (2)$$

From these measurements, the  $\tau_c$  value was estimated to be 0.16 ms at 240 K. This compares favorably with the value for  $\tau_c$  (0.2 ms) obtained from the line shapes, described in the previous section. Not only are these values comparable to each other, but they also agree very well with ionic conductivity estimates.<sup>5</sup>

The temperature variation of  $T_1$  and  $T_2$  below 230 K is markedly different from that observed at higher temperatures. The temperature variation of  $T_1$  below 230 K is nearly independent of temperature and, if thermally activated, would correspond to a very low  $E_a$  value (0.02 eV). The temperature variation of the CPMG  $T_2$  below 230 K is also similar to that of  $T_1$ , having a small activation energy (about 0.06 eV) between 230 and 150 K, which is consistent with ionic conductivity results.<sup>5</sup> However, at around 250 K  $T_2$  exhibits what appears to be a jump discontinuity, which is suggestive of a structural phase transition.

With regard to the possible existence of a structural phase transition in proustite below 250 K, a Raman spectral study observed a splitting of one of the low-frequency phonon modes below 210 K.<sup>6</sup> Both an inflection in the temperature dependence of the phonon frequency in Brillouin scattering<sup>8</sup> and a change in the optically induced acoustic attenuation in an ultrasonic study<sup>7</sup> were observed at around 210 K. Al-

though these anomalies were interpreted to indicate a broad phase transition around 210 K, there were other studies that did not find any evidence for a phase transition near this temperature.  $^{75}\text{As}$  NQR studies<sup>11,12</sup> did not report any anomaly in the NQR frequency between 300 and 60 K. Since the NQR frequency sensitively depends on the positions of atoms which normally change in a phase transition, the absence of any sudden change in the NQR frequency strongly suggests no significant phase transition between 300 and 60 K. Furthermore, a more recent Raman study<sup>10</sup> has suggested that a possible leak-through component may be responsible for the additional phonon splitting reported earlier,<sup>6</sup> thereby eliminating some of the evidence for a phase transition. Neutron and x-ray-diffraction studies<sup>26</sup> also did not find any change in the diffraction pattern between 61 K and room temperature.

The present NMR study definitely finds significant changes in the behavior of proustite at around 240 K, as evidenced by the marked changes observed in the temperature variations of the line shape,  $T_1$ , and  $T_2$ . However, it is unlikely that these changes are due to a structural transition, considering that the more sensitive NQR and x-ray-diffraction studies did not observe any structural rearrangements in this temperature region. In view of these observations, our  $^{109}\text{Ag}$  NMR data in proustite imply a significant change in the motional behavior of  $\text{Ag}^+$  near 240 K rather than a structural phase transition.

### C. Temperature dependences of the Hahn and CPMG spin-echo decays

A comparison of the Hahn spin-echo decay with the corresponding CPMG spin-echo decay in proustite has interesting features between 180 and 55 K. Above 180 and below 55 K the Hahn spin-echo decay is identical to the CPMG decay, and the magnetization decay in both cases is describable by a simple exponential dependence of time. However, at intermediate temperatures (between 180 and 55 K) the Hahn spin-echo decay is considerably shorter than the CPMG spin-echo decay, and decays with an exponent proportional to  $\tau^3$ ,

$$M(t) \propto \exp[-k\tau^3], \quad (3)$$

where  $\tau$  is the delay between that  $\pi/2$  and  $\pi$  pulses. Figure 4 illustrates these observations at two different temperatures. Such an observation is consistent either with slow modulation wave diffusion<sup>20,21</sup> or with slow atomic jumps between chemically inequivalent sites. However, slow modulation wave diffusion can be ruled out above  $T_I$  (60 K), since there should be no modulation wave in the paraelectric phase.

In order for the Hahn spin-echo decay time to be shorter than  $T_2$ , the average spin precession frequencies before and after the  $\pi$  pulse must be different, so that the average loss of phase before the  $\pi$  pulse is not completely reversed. The  $\tau^3$  behavior of the Hahn spin-echo decay has in the past been observed only in the presence of a magnetic-field gradient or for a quadrupolar nucleus in an inhomogeneous internal electric-field gradient. Such observations for a dipolar nucleus like  $^{109}\text{Ag}$  are unusual in that neither of the above types of gradients is present. Furthermore, such behavior above  $T_I$  (60 K) cannot be associated with the presence of any modulation wave motion [as was earlier observed below

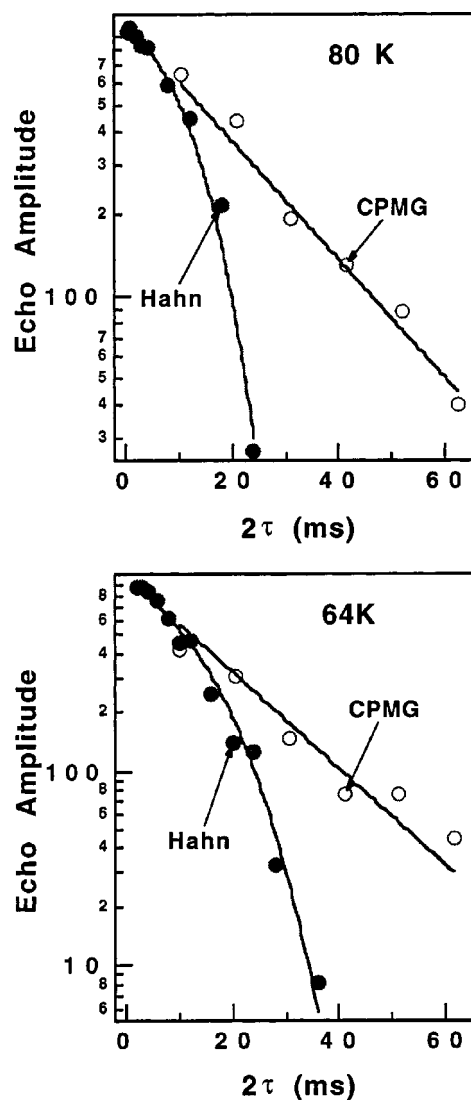


FIG. 4. Comparison of Hahn and CPMG spin-echo decays at 80 and 64 K in proustite.

$T_I$  in barium sodium niobate<sup>20</sup> and in  $\text{Rb}_2\text{ZnCl}_4$  (Ref. 21)], since the modulation wave does not exist in the paraelectric phase above  $T_I$ . However, since the line shape in this temperature range indicates a significant chemical shift difference between the Ag sites, a possible explanation is that the  $\text{Ag}^+$  ions are executing slow hopping motions between the chemically inequivalent sites.

If the chemical shift gradient  $g$  is known, the effective diffusion constant  $D$  characterizing the Ag ion jump motions can then be estimated by fitting the Hahn spin-echo decay to Eq. (1) over the range (180–60 K) where the Hahn decay is shorter than the CPMG decay. It may appear surprising to use a diffusion coefficient to characterize jumping between two sites. However, if the NMR frequency is sufficiently different between the two sites and if the mean jump time is comparable to the time between the  $\pi/2$  and  $\pi$  pulses in the Hahn echo sequence, then the magnetization will decay according to an equation like Eq. (1).

The effective “gradient”  $g$  due to chemical shift (i.e., the spatial variation of the NMR frequency) can be estimated from NMR data and from a knowledge of the crystal structure.<sup>23</sup> From the crystal structure of proustite, the dis-

tance between two neighboring Ag sites is about 3.2 Å. From the NMR line shape, the frequency difference between neighboring Ag sites is about 500 Hz at 64 K [shown in Fig. 1(a)]. Thus, the frequency gradient  $g$  is 500 Hz/3.2 Å. By fitting curves like those in Fig. 4 to Eq. (1), the effective  $D$  value was estimated to be about  $5.6 \times 10^{-14}$  cm<sup>2</sup>/s, which is an extremely small value. One can also estimate the effective  $D$  value from

$$D = a^2/6\tau_c, \quad (4)$$

where  $a$  is the distance between neighboring sites (3.2 Å) and  $\tau_c$  is the jump correlation time. Since the  $\tau_c$  value determined from the line-shape measurements is about 5 ms at 80 K, the  $D$  value at 80 K is estimated from Eq. (4) to be about  $8.5 \times 10^{-14}$  cm<sup>2</sup>/s, which agrees with the value obtained by applying Eq. (1) to the Hahn decay.

Within the incommensurate phase, the Hahn spin-echo decay tends towards the CPMG spin-echo decay as the temperature is lowered below 60 K until, at 55 K the Hahn and CPMG spin-echo decays become almost the same. The lengthening of the Hahn spin-echo decay time constant on cooling into the incommensurate phase probably reflects a further slowing down of the motions until they are too slow to affect the Hahn echo. The magnetization decay for the case of slow diffusion of a one-dimensional incommensurate modulation wave has been solved for arbitrary dependence of the NMR frequency  $f$  on the cosine of the phase and shown<sup>20</sup> to be

$$M(x, 2\tau) = M(x, 0) \exp[-2\tau/T_2] \exp[-2Df' \sin^2 \phi(x) \times (d\phi/dx)^2 \tau^3/3], \quad (5)$$

where  $\phi(x)$  is the phase of the modulation wave,  $f(\cos \phi)$  represents the dependence of the NMR frequency on  $\cos \phi$ , and  $f'$  is the first derivative of  $f$  with respect to  $\cos \phi(x)$ . Our

observations of a Hahn decay that is shorter than the CPMG decay and that has an exponential dependence on  $\tau^3$  suggests that modulation wave motions are being observed between 60 and 55 K. However, an unambiguous proof of this would require a two-dimensional exchange or exchange-difference measurement.<sup>27</sup>

#### IV. CONCLUSIONS

Our <sup>109</sup>Ag NMR line shape and relaxation time measurements in proustite indicate a significant change in the Ag<sup>+</sup> motional characteristics near 240 K. Above 240 K, diffusion motions of Ag<sup>+</sup> ions between sites corresponding to AsS<sub>3</sub> pyramids in different planes seem to occur and are characterized by correlation times which are much shorter than the reciprocal of the frequency difference between different chemically shifted Ag atoms. Below 240 K, the Ag motions seem to be confined to within a single pyramid and the intrasite hopping is much slower than the NMR time scale. Even though these motions are too slow to narrow the NMR lines below 180 K they can still be detected via their effect on the Hahn spin-echo decay, which is still shorter than the CPMG decay between 180 and 55 K. The present observation of  $\tau^3$  behavior in the Hahn decay constitutes the first report of such spin dephasing due to ultraslow atomic diffusion in the presence of a spatially varying chemical shift.

#### ACKNOWLEDGMENTS

This research was supported by U.S. National Science Foundation under NSF Grant No. DMR-9624962. We are indebted to Professor R. Blinc for many helpful discussions and for providing us with the proustite single crystal. We are also grateful to Dr. P.-H. Chan for his assistance in setting up the initial experiments.

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