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NMR study of a temperature-induced structural transition in $ZrBe_2D_x$

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Abstract

We have studied the motion of D atoms in $ZrBe_2D_{1.56}$ and $ZrBe_2D_{1.4}$ using deuterium NMR and observed a temperature-induced structural transition near 240 K. By comparing the behavior of hydride and deuteride samples with the same concentration ($x=1.4$), the absence of a transition in the hydride is shown to be an isotope effect. Above 240 K, the deuterium relaxation times T_1 and T_2 behave as expected from proton data in $ZrBe_2H_{1.4}$. However, on decreasing the temperature below 240 K, T_2 decreases rapidly and T_1 increases rapidly, indicating that the D atom mobility is dramatically reduced. Above the transition temperature, the spectrum shows a quadrupolar doublet splitting of order 1 kHz, reflecting a small motionally averaged electric field-gradient (EFG) at the D atoms. Upon cooling below 240 K the line broadens rapidly, revealing a large distribution of quadrupolar splittings and EFGs at the individual sites. Thus substantial variations exist between the D-atom sites, despite their nominal equivalence in the neutron diffraction-determined structure. We suggest that the strong Be–H (Be–D) repulsion generates substantial Be displacements near vacant D-atom sites. The probable nature of the transition is discussed from the point of view of ordering of D-atom vacancies.

Keywords: Intermetallic compound; Deuterium; Diffusion; Two-dimensional diffusion; Structural transition; Isotope effect; NMR

1. Introduction

The intermetallic compound $ZrBe_2$ crystallizes in a hexagonal AlB_2-type structure [1]. The crystal lattice consists of alternate layers of zirconium (Zr) and beryllium (Be) atoms, with one Zr and two Be atoms at (0,0,0), (1/3,1/3,1/2) and (2/3,2/3,1/2), respectively in the unit cell [1]. This material absorbs up to 1.5 hydrogen (H) or deuterium (D) atoms per unit cell at room temperature and one atmosphere of hydrogen pressure [2]. Neutron diffraction indicates that the D atoms reside in the hexagonal Zr planes directly above and below each Be atom, i.e. at the centers of the triangles formed by the Zr atoms (*2c* sites) [1,2]. Theoretical full occupation corresponds to two H atoms per formula unit. Deuteriding to $x=1.5$ ($ZrBe_2D_{1.5}$) results in a 7.3% expansion along the *c* axis and a 2.7% contraction along the *a* axis, with no change in crystal symmetry [1,2]. Westlake suggested that the H (D) atoms occupy either of the slightly off-plane *4h* sites [3]. These sites occur in pairs, only 0.064 Å above and below each *2c* site (i.e. displaced along the *c* axis). Fast local motion between the sites at room temperature may average the position to *2c*, as seen by neutron diffraction [1,2,4].

At room temperature H atoms are quite mobile in the hydride with ~10^8 hops/s between neighboring *2c* sites [5]. The considerable expansion of the *c* axis upon deuteriding indicates an effective Be–D (or Be–H) repulsion. This repulsion is expected to affect the D diffusion, with the intervening layer of Be atoms potentially blocking D atoms from hopping between planes. Indeed, NMR studies of $ZrBe_2H_{1.4}$ show strong evidence of such two-dimensional diffusion. The frequency dependence of the spin lattice relaxation rate T_1^{-1} in both static field [6] and field-cycling [7] measurements and pulse field-gradient diffusion measurements [7] unambiguously demonstrate the 2-D character of the motion.

A powder neutron diffraction study of $ZrBe_2D_{1.5}$ [8] reported a temperature-induced structural change below 250 K. Superlattice peaks appeared upon cooling; a model with occupation of the *4h* sites resulted in improved Rietveld refinements at 12 K. The study suggested an order–disorder-like change in the deuterium site occupancy from *2c* to *4h* on cooling.

We note that previous hydrogen NMR studies of $ZrBe_2H_{1.4}$ reported no evidence of a phase transition [5–7]. In particular, the T_1 and $T_{1\rho}$ data extending from 115 to 400 K are well described by a single model [5]. The

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different behaviors of the deuteride and hydride partly motivated this study. The present paper provides clear NMR evidence of a structural transition in $ZrBe_2D_x$ ($x=1.4$ and 1.56). We propose that the observed transition involves ordering of the D atom vacancies.

2. Experimental

The preparation procedures of the powder sample have been reported previously [2]. Measurements were made in Oxford superconducting magnets at fields of 4.4 and 8.0 T. Deuterium nuclear spin relaxation rates were measured using a computer-controlled home-built pulsed NMR spectrometer and a Chemagnetics CMX360 spectrometer. T_1 was measured using a saturation-recovery-inspection method. Inspection of the partially recovered longitudinal magnetization was done by a $\pi/2$–τ–$\pi/2$ echo generating pulse sequence with short, fixed τ. T_2 was measured with a simple $\pi/2$–τ–$\pi/2$ echo sequence. Many of the recoveries/decays were non-exponential; the reported relaxation time was defined as the $1/e$ point of the recovery–decay curve.

The temperature was varied using flowing N_2 gas or air controlled by a thermostat. The temperatures were steady to within ±0.5 K and were measured using a type-T (copper–constantan) thermocouple with a room temperature reference.

3. Results and discussion

The intrinsic (homogeneous) spin dephasing time constant T_2 was measured for $ZrBe_2D_{1.56}$ and $ZrBe_2D_{1.4}$ in the temperature range 175–320 K. Fig. 1 shows the relaxation rate T_2^{-1} as a function of reciprocal temperature for the two samples at 52 MHz. In both samples a sharp rise in T_2^{-1} is observed below 240 K. Within a span of 30–40 K, T_2^{-1} increases by a factor of 40. The onset of this transition appears at a slightly higher temperature for $ZrBe_2D_{1.4}$ than $ZrBe_2D_{1.56}$. The rapid increase in T_2^{-1} points to a dramatic reduction in the D-atom mobility in both samples below 240 K. Between 230 and 240 K, the T_2 decay showed biexponential behavior indicating coexistence of two phases. For the hydride, T_2 data extending only down to 235 K are available but do not indicate a phase transition [6]. Rotating-frame relaxation time $T_{1\rho}$ data are available [5] over the wider range of 140–320 K. The T_1 and $T_{1\rho}$ data of Ref. [5] are described well by a model with a single correlation time describing the motion, with a constant activation energy, indicating that no transition occurs in $ZrBe_2H_{1.4}$.

Although the interactions being modulated in the two cases are different (magnetic dipole for hydrogen and electric quadrupole for deuterium), the relaxation rates are direct measures of the rates of hopping motion. The slopes of the straight lines drawn in Fig. 1 through the deuterium T_2^{-1} data can be expressed in energy units, as apparent activation energies. These values are 0.73 and 0.54 eV for deuteride samples with $x=1.4$ and $x=1.56$, respectively, while the activation energies for the proton T_2^{-1} data [6] (only down to 235 K) and T_{1D} data [5] (down to 140 K) are 0.18 and 0.20 eV, respectively. Thus the temperature dependence of the rate of atomic hopping for the deuteride samples is much stronger than for the hydride, indicating that a transition occurs in the deuteride but not in the hydride.

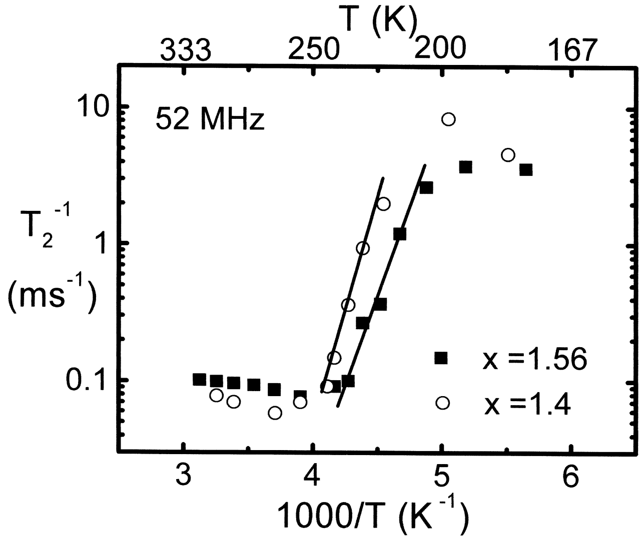

Fig. 1. Comparison of deuterium intrinsic spin dephasing rate T_2^{-1} in $ZrBe_2D_x$ for $x=1.56$ (■) and $x=1.4$ (○). The rapid increase below 240 K is due to a strong decrease in deuterium mobility, resulting from the phase transition.

T_1 was measured for $ZrBe_2D_{1.56}$ at 52 MHz and 29 MHz and for $ZrBe_2D_{1.4}$ at 52 MHz. Fig. 2a compares the longitudinal relaxation rate T_1^{-1} for $ZrBe_2D_{1.56}$ at the two frequencies with the proton data for $ZrBe_2H_{1.4}$ at 35 MHz published previously [5]. The lines drawn through the data at temperatures below the T_1^{-1} maxima serve as guides to the eye. The deuterium T_1^{-1} decreases more rapidly than the proton T_1^{-1} below 240 K, as shown by the steeper slopes of the deuteride data, again suggesting a transition in the deuteride. Fig. 2b compares the T_1^{-1} data as a function of reciprocal temperature for the two deuteride concentrations. The similarity of results for the two deuteride samples, one of which has the same $x=1.4$ concentration as the hydride studied earlier [5], indicates that the presence of the transition in the deuteride (versus its absence in the hydride) is an isotope effect. We note that phase transitions in C-15 Laves phase hydrides $HfV_2H_x(D_x)$ and $ZrV_2H_x(D_x)$ [9] were detected by rapid changes in T_1 near the transition temperature.

Fig. 3 shows deuterium NMR spectra for $ZrBe_2D_{1.4}$ at decreasing temperatures. The spectrum at 295 K is shown at two different frequencies (29 and 52 MHz) while the

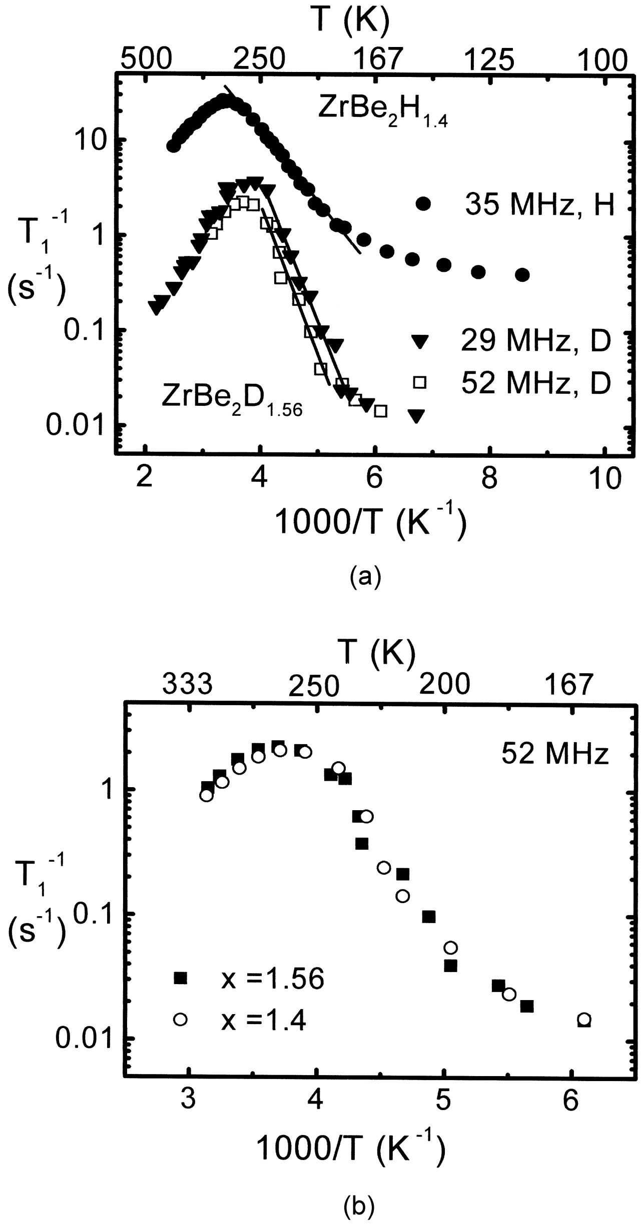

Fig. 2. (a) Comparison of longitudinal relaxation rate T_1^{-1} for $ZrBe_2H_{1.4}$ (proton) at 35 MHz (●) and $ZrBe_2D_{1.56}$ (deuterium) at 29 MHz (▼) and 52 MHz (□). (b) Comparison of deuterium longitudinal relaxation rate T_1^{-1} for $ZrBe_2D_x$ for $x=1.56$ (■) and $x=1.4$ (○).

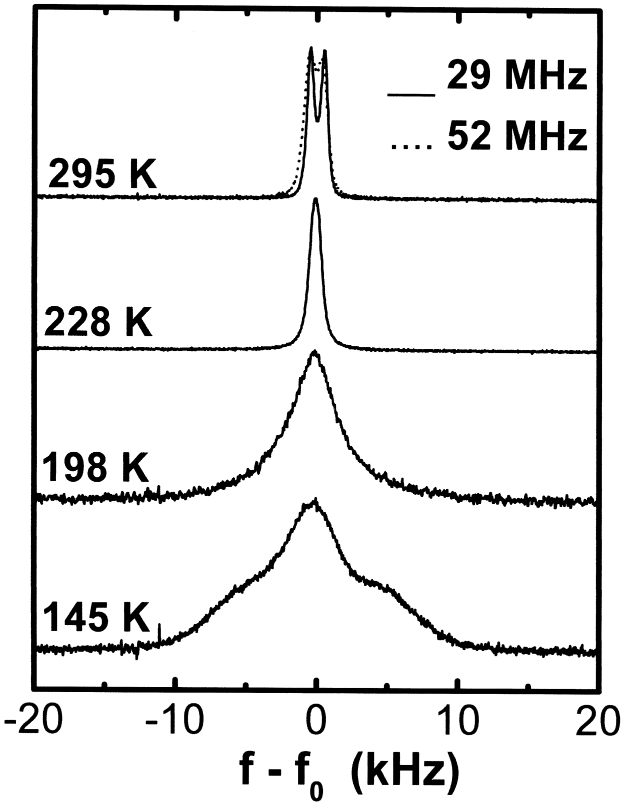

Fig. 3. Temperature dependence of deuterium NMR spectra for $ZrBe_2D_{1.4}$ at 29 MHz (———). Spectrum at 295 K obtained at 52 MHz (- - -).

other spectra were obtained at 29 MHz. The spectral lineshapes are dominated by quadrupolar interactions [10,11], as D–D spin dipolar interactions are weak and deuterium Knight shifts (like proton Knight shifts) are small [12–14]. At 295 K, motional averaging yields a Pake doublet with a small splitting (~1 kHz), independent of the NMR field and frequency, as expected for a quadrupolar interaction.

We note that a Pake doublet refers here to the spectrum arising from a quadrupole moment interacting with an electric field-gradient (EFG) at the lattice site. Unlike the original observation of Pake [16], this does not involve dipole–dipole interaction between nuclear spins. There is a formal analogy between a single spin-1 with quadrupole interaction and two spins-1/2 coupled by mutual dipolar interaction.

The poorer resolution of the doublet at the higher frequency is probably due to magnetic susceptibility of the powder particles [15]. The splitting results from a small but non-zero EFG average over all occupied sites. We note that there is no symmetry requirement for the EFG to average to zero over the sites of a hexagonal lattice. Below 295 K, the splitting depends weakly on temperature; in the 228 K spectrum in Fig. 3, no splitting is evident. At lower temperatures a single line is observed which broadens rapidly with decreasing temperature; the Lorentzian-like lineshape indicates a slowing of the motion, as does the increase in T_2^{-1} (Fig. 1).

At and below 145 K, a temperature independent spectrum occurs, showing that motional averaging has ceased (no motions on the NMR time-scale, of order 10^{-3} s). The low temperature spectrum arises from a superposition of Pake doublets from sites with a broad distribution of individual EFGs. It is remarkable that the distribution of EFGs is so large, because the *2c* sites of the ideal, fully occupied structure ($x=2$) are completely equivalent and should have identical EFGs (both in magnitude and tensor direction). This statement is equally true of the *4h* sites in the ideal structure. Thus, in the ideal $x = 2$ structure, no motional averaging of the quadrupolar interaction would occur. Therefore, the much broader spectrum at 145 K than at 295 K is powerful evidence that the individual sites have a large range of EFGs, while the average EFG over the sites is quite small. Here we make the reasonable assumption that the principal effect of lowering the temperature is cessation of motional averaging. We note that the dipolar broadening in the deuterium spectrum in the rigid lattice limit can be estimated as 2 kHz, by scaling [10] the proton second moment taken from fits to T_1^{-1} data [5,6]. This contribution is much smaller than the observed linewidth, confirming that the line is broadened primarily by electric quadrupole interaction.

What is the source of the large distribution of EFGs over the D-atom sites? We propose that D-atom vacancies generate local structural distortions, primarily by displacements of the two neighboring Be atoms. For example, due to effective Be–D repulsion, a Be atom near a D vacancy would be displaced toward it. The position of a Be atom should thus be strongly coupled to the neighboring D-atom positions and to D-site occupancies by Be–D repulsion. This is supported by the large displacement factors (mean-squared displacements from the ideal positions) of both Be and D atoms in the neutron diffraction report [8].

We propose that the observed decrease in deuterium mobility and the observation of superlattice peaks in the neutron diffraction study [8] indicate an ordering of the D-atom vacancies below 240 K. In this model, the D-atom vacancies interact through displacements of the intervening and nearby Be atoms. Ordering of the D-atom vacancies would result in a periodic dimpling of the Be atom layers and might be observable by ^{9}Be NMR. We note that there are two 'types' of Be atoms expected, those with two deuterium neighbors (one above and one below) and Be atoms with one deuterium neighbor and one neighboring D-atom vacancy. Location of two D-site vacancies at a single Be atom would appear to be energetically unfavorable. ^{9}Be NMR experiments are currently underway to test this hypothesis of D-atom vacancy ordering.

4. Conclusions

A temperature-induced transition in $ZrBe_2D_x$ ($x = 1.4$ and 1.56) has been observed by deuterium NMR. For temperatures below 240 K, a rapid decrease in D-atom mobility is signaled by rapid increases in T_2^{-1}, T_1 and linewidth. The apparent absence of a similar transition in $x = 1.4$ hydride is an isotope effect. The low-temperature spectrum reveals a large distribution of EFGs at the deuterium atoms, despite the identical EFGs expected in the ideal, fully-occupied ($x = 2$) structure. The large EFGs are believed to result from Be and D displacements, which are coupled to each other and to D-atom vacancies by Be–D repulsion. This mechanism may result in an order–disorder transition of the D-atom vacancies, which would be in accordance with the observed strong decrease in deuterium mobility.

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