Anomalous transverse-spin relaxation in $ZrCr_2H_x$

Ronald Dean Stoddard,* John J. Balbach,† and Mark S. Conradi
Department of Physics, CB 1105, Washington University, St. Louis, Missouri 63130-4899

A. V. Skripov
Institute of Metals Physics, Urals Branch of the Academy of Sciences, Ekaterinburg 620219, Russia
(Received 14 August 1998)

A detailed examination of the transverse nuclear-spin relaxation is presented for hydrogen in $ZrCr_2H_x$ with $x=0.2$, 0.3, and 0.5. One unusual aspect of the transverse relaxation is the relatively large linewidth at high temperatures, where the dipolar interactions are fully averaged. This residual linewidth varies with external field strength more slowly than linearly, indicating the role of ferromagnetic impurities in addition to the more common susceptibility broadening. Spin echoes yield a T_2 measurement which substantially defeats the large residual linewidth. However, a second unusual aspect is that above 170 K, T_2^{-1} reverses slope and starts to increase with increasing temperature, going through a maximum near 225 K. In the 170–225 K region, the measured T_2 varies with pulse spacing of the Carr-Purcell pulse train. The behavior of T_2^{-1} cannot be explained by H-atom diffusion through field gradients from the particles' magnetization. The sample appears to become inhomogeneous above 170 K on a length scale of ~ 300 Å, suggesting an unexpected phase transition in these materials. [S0163-1829(99)06805-8]

I. INTRODUCTION

The Laves-phase metal-hydrogen system $ZrCr_2H_x$, with $x=0.2$–0.5, has remarkably rapid hydrogen diffusion. The proton NMR line is almost fully narrowed by 80 K, an unusually low temperature.[1,2] Pulsed field gradient (PFG) measurements of hydrogen diffusion find a non-Arrhenius temperature dependence of diffusivity.[3] The very low apparent activation energy at low temperatures suggests a quantum mechanical aspect to the diffusion.

The proton spin-lattice relaxation rate (T_1^{-1}) in the laboratory frame has been thoroughly studied for $ZrCr_2H_x$.[1,2] The T_1^{-1} data can be described in terms of a distribution of activation energies for hydrogen diffusion. However, as has been noted,[2] the T_1^{-1} data for $ZrCr_2H_x$ are also consistent with a coexistence of two types of H motion with different frequency scales.

Recently, measurements of $T_{1\rho}^{-1}$, the spin-lattice relaxation rate in the rotating frame, provided evidence that the mean-square strength of the fluctuating dipolar fields that drive spin relaxation increases with decreasing temperature.[4] This indicates an existence either of a change in local hydrogen ordering or of rapid local motions that partially average the dipole interactions. Direct evidence for a rapid localized motion of H atoms in $ZrCr_2H_x$ has been found in recent quasielastic neutron-scattering measurements.[5] The microscopic picture of H motion in $ZrCr_2H_x$ appears to be similar to that found[6] in the related Laves-phase system TaV_2H_x. In particular, the fraction of H atoms participating in the rapid localized motion strongly increases with increasing temperature; this behavior may qualitatively explain the $T_{1\rho}^{-1}$ results.

However, to our knowledge, there have been no quantitative studies of the *transverse* relaxation times T_2 and T_2^* in $ZrCr_2H_x$, outside the observation of a narrowed line at 80 K. Thus we report here a thorough study of transverse relaxation in $ZrCr_2H_x$, with $x=0.2$, 0.3, and 0.5. We focus on two aspects. First, at temperatures such that the dipole interactions are fully averaged, a large residual linewidth remains. In metal hydrides,[7,8] this is not uncommon[9] and generally arises from the magnetic susceptibility of the metals and the array of different particle shapes and their orientations to the external magnetic field[10] (rf skin depth considerations dictate the study of powders). However, in $ZrCr_2H_x$, the residual linewidth is unusual in varying more slowly than linearly with the field strength.

The second and main focus of this report is on the relaxation rate T_2^{-1} determined with two-pulse spin echoes and spin-echo trains.[11,12] The temperature variation of T_2^{-1} reverses at high temperatures and exhibits a maximum. In this region, the apparent T_2^{-1} is different when measured with single-echo vs multiple-echo[13,14] methods and depends on the pulse spacing in the multiple-echo method.

It is valuable to detail the behavior of T_2^{-1} in other, more ordinary systems. In $ZrBe_2H_{1.4}$, the H atom diffusion is restricted to planes[15] perpendicular to the c axis.[16,17] However, the T_2^{-1} behavior is typical and can be explained simply (see Fig. 4 of Ref. 16). At low temperatures T (off the graph), T_2^{-1} is expected to attain its limiting, rigid-lattice value.[12] At higher temperatures, T_2^{-1} decreases due to motional averaging of the dipolar fields. As T increases further, eventually T_2^{-1} stops decreasing and becomes nearly constant. This change in behavior is due to H atom diffusion through the field gradient G inside each particle.[9,16] At higher external field strengths, the onset of this additional transverse damping occurs at a lower temperature—the internal gradients are caused by susceptibilities, so the gradients are proportional to the external field. The larger gradients lead to increased diffusive transverse relaxation, as in Hahn's formula[12] for the damping in a uniform field gradient, $\exp(-2\gamma^2G^2D\tau^3/3)$. (Note that *uniform* gradients are not present in the small metal particles.) Use of the Carr-Purcell-Meiboom-Gill multiple-echo sequence[13,14] greatly reduces

 ©1999 The American Physical Society

the diffusion-in-a-gradient effect, allowing the true T_2 to be measured to higher temperatures. All these effects are apparent for T_2^{-1} for $ZrBe_2H_{1.4}$.

The present study of $ZrCr_2H_x$ has two motivations. First, $ZrCr_2H_x$ is unusual amongst metal-hydrogen systems (see above) in having substantial H mobility at low temperatures and a non-Arrhenius temperature dependence of H diffusivity. Second, because of the large H mobility already at low temperatures, the behavior of the transverse spin-relaxation rate T_2^{-1} can be followed over a wide range of temperatures.

II. EXPERIMENTAL

The $ZrCr_2$ was prepared and hydrided at the Institute of Metals Physics, Ekaterinburg. The details of the sample preparation have been described previously.[1,2] The samples used here are all in the C15 crystallographic structure,[18] with $x=0.2$, 0.3, and 0.5. The $x=0.3$ material was from one batch of $ZrCr_2$,[1] while the $x=0.2$ and 0.5 materials were from a second $ZrCr_2$ batch.[2]

The NMR measurements were performed in an iron-core magnet with flux stabilization and ^{19}F NMR regulation. Most of the work below 125 K used a research dewar with variable temperature capability, with the sample immersed in flowing He gas. Thermometry was provided by a calibrated carbon-in-glass resistance thermometer (for $T<80$ K) and a type-T (copper-constantan) thermocouple (primarily for $T>80$ K). Most work above 125 K used a different NMR probe, with the sample bathed in flowing, temperature controlled N_2 gas (obtained by boiling liquid N_2). Here a type-T thermocouple was used to measure temperature.

The transverse dephasing time T_2^*, essentially the reciprocal of the linewidth, was determined directly from the free induction decay (FID) $F(t)$. Regardless of the shape of the decay, T_2^* may be consistently defined as

$$T_2^* \equiv \int_0^\infty F(t)dt/F(0).$$

In practice, the time zero is shifted to the first time uncorrupted by receiver blocking and recovery, about 10 μs at 21.25 MHz. The long-time limit of the integral is a compromise between capturing all of the FID and minimizing the amount of noise included in the integral. Of the many possible definitions of T_2^*, the one above gives strong weight to any long T_2^* (narrow frequency) components. In all cases, the dephasing rate T_2^{*-1} obtained with a water sample was 10^{-2} or less than any of the values reported here for $ZrCr_2H_x$. That is, the field inhomogeneity of the magnet itself was negligible.

Spin echoes were used to determine T_2. The two-pulse[11] technique (90°-τ-180°-τ-echo, with τ varied) as well as the Carr-Purcell-Meiboom-Gill (CPMG) method,[12–14] resulting in a train of echoes, were used. For long T_2 with short T_2^*, the data acquisition recorder was synchronized with the CPMG pulse sequence, to guarantee that the echo *peaks* were recorded. In general, the echo decays deviated only modestly from single exponential. The T_2 value reported is the time for which the echo amplitude has decayed by $1/e$.

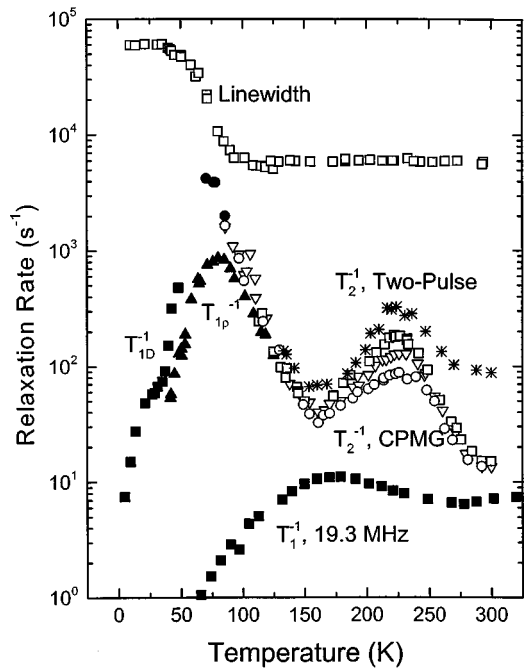

FIG. 1. Overview of relaxation rate data for $ZrCr_2H_{0.5}$ all at 21.3 MHz, except for T_1^{-1} (solid squares, at bottom). Note the limited extent of line narrowing in the T_2^{*-1} linewidth data (open squares, top of figure), due to magnetization of the powder sample. Spin-echo measurements of T_2^{-1} are presented, both from two-pulse echoes (*) and from CPMG echo trains (□, △, ○, and ●, denoting values of the pulse spacing 2τ of 200, 100, 60, and 30 μs, respectively). Note the anomalous peak in T_2^{-1} near 225 K. The relaxation rate along the rf field $T_{1\rho}^{-1}$ is presented (▲) for a 39 kHz nutation frequency. The solid squares at left are T_{1D}^{-1}, the decay rate of dipolar spin order.

III. RESULTS AND DISCUSSION

A. Overview

To provide an overview of spin relaxation in $ZrCr_2H_x$, the relaxation rates T_2^{*-1}, the linewidth from free induction decays; T_2^{-1}, the dephasing rate of two-pulse echoes and Carr-Purcell-Meiboom-Gill echo trains; and T_1^{-1}, the rate of spin-lattice relaxation are presented in Fig. 1 for $x=0.5$. In addition, the rotating-frame relaxation rate $T_{1\rho}^{-1}$ (solid triangles) and the decay rate of dipolar order, T_{1D}^{-1} (solid squares), are also displayed.

The onset of motional averaging from H atom motions is evident at 50 K, with the linewidth T_2^{*-1} decreasing at higher temperatures. By 100 K, the linewidth attains a constant value, as discussed below. Nevertheless, T_2^{-1} from echoes continues to decrease, indicating that the linewidth above 100 K is due to some *inhomogeneous broadening*.[19] As expected, $T_{1\rho}^{-1}$ and T_2^{-1} are essentially equal on the high-temperature side of the $T_{1\rho}^{-1}$ maximum.[12] Above 170 K, T_2^{-1} values measured by the spin-echo methods increase and pass through a maximum. This anomalous behavior of T_2^{-1} is substantially the subject of the present paper.

B. Linewidth

The T_2^{*-1} linewidth data are presented in greater detail in Fig. 2. In Fig. 2(a), the linewidth for $x=0.5$ is shown for

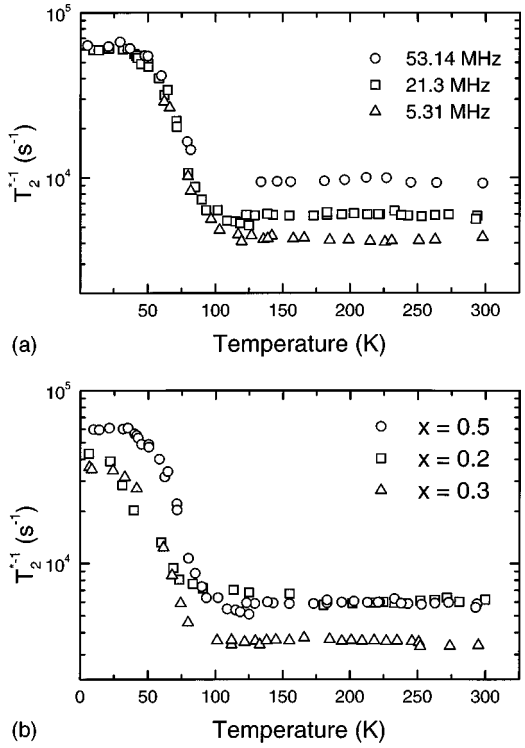

FIG. 2. Linewidth data (T_2^{*-1}, from free induction decays) for $ZrCr_2H_x$. (a) For $x=0.5$ at three different frequencies and fields (1250, 5000, and 12 500 G, bottom to top). The high-temperature limiting linewidth increases with field strength, but much more slowly than linearly. (b) Linewidth data at 21.3 MHz for three compositions. The high-temperature limiting values are the same for $x=0.2$ and 0.5, but smaller for $x=0.3$.

three field strengths and resonance frequencies, spanning a decade in range. At low temperatures, the linewidths are independent of field, demonstrating that dipolar interactions dominate here. Because the metal nuclei have nuclear spins with small magnetogyric ratios and low abundances, the dipolar interaction is mainly proton-proton.

Above approximately 100 K, the linewidth is independent of temperature and much larger than the spin-echo T_2^{-1}. Thus, some inhomogeneous broadening dominates the linewidth at the higher temperatures. A very common source of excess linewidth in metal hydrides is distortion of the otherwise uniform external field by the magnetic susceptibility of the material.[9] The powder particles are of various shapes and have random orientations relative to the field. Thus, the field inhomogeneity is directly proportional to the magnetization M of the material. Often, M is *induced magnetization* with $M=\chi H$; in that case the limiting linewidth is expected to be linear in the external field.[10] But the linewidth in Fig. 2(a) increases much more slowly, varying only by a factor $\simeq 2.2$ for a factor of 10 change in field. We recall that the inhomogeneity of the electromagnet itself is completely negligible on the scale of Fig. 2.

A simple scenario that explains the field dependence in Fig. 2(a) is to postulate that the sample contains some ferromagnetic material. Presumably, at all the fields used here, the ferromagnetic regions are saturated, producing a constant magnetization, M_0. Thus, the sample magnetization M follows $M=\chi H+M_0$. Therefore, the inhomogeneous linewidth should likewise have constant and linear terms,

$$T_2^{*-1}=A+BH_0, \tag{1}$$

with H_0 the external field strength. The data of Fig. 2(a) fit very well to Eq. (1) with $A=3.5\times 10^3$ s^{-1} and $B=0.48$ s^{-1}/G. Magnetization measurements at 295 K (not shown) using a superconducting quantum interference device based system detect the presence of a weak ferromagnetic impurity, as indicated by $M_0\neq 0$ in the above equation.

Further evidence concerning the origin of the high-temperature limiting linewidth is presented in Fig. 2(b). There the linewidth at 21.3 MHz (5000 G) is presented for three different compositions x. The $x=0.2$ sample has a smaller low-temperature linewidth than for $x=0.5$, as expected from the weaker average like-spin interactions. But the high-temperature inhomogeneous linewidths are similar for $x=0.2$ and 0.5 and smaller for $x=0.3$. Now the $x=0.2$ and 0.5 hydrides were prepared from one batch of $ZrCr_2$ metal, while $x=0.3$ was from a different batch. Evidently, at least part of the limiting linewidth is from impurities which originate in the metal material prior to hydriding.

C. Additional T_2^{-1} at high temperatures

The T_2^{-1} data from the region of additional spin dephasing is detailed in Fig. 3(a) for the $x=0.5$ sample at three different resonance frequencies and field strengths. At and above 170 K, T_2^{-1} becomes larger than the smooth extrapolation of the lower temperature data and passes through a maximum before decreasing again. The additional dephasing is larger at higher fields and depends on the CPMG (Refs. 13 and 14) pulse spacing 2τ. In Fig. 3(b), T_2^{-1} from CPMG echo trains is presented for $x=0.2$, 0.3, and 0.5, all at 21.3 MHz. The maximum additional relaxation increases markedly with increasing H-atom content. The T_2^{-1} data for a $ZrCr_2H_{0.4}$ sample with the hexagonal Laves (C14) structure (data not shown) are very similar to the data for the C15 structured sample with $x=0.3$. Clearly, H-atom content is a key variable for the phenomenon.

To understand the T_2^{-1} behavior above 170 K, we first rule out certain mechanisms. Could the retrograde behavior of T_2^{-1} from 170 to 220 K indicate that H-atom motions are *slowing down* with increasing temperature? Such a proposal has been made,[20] but for different metal-hydride systems to explain high-temperature spin-lattice relaxation.[21] However, the directly measured diffusion coefficient D increases monotonically in this range.[3] Furthermore, dephasing from the stochastically modulated dipole interactions is independent of field strength and independent of the CPMG pulse spacing 2τ. Thus, we exclude a nonmonotonic rate of atomic motions with temperature.

The additional relaxation rate T_2^{-1} displays a *monotonic* dependence on the hydrogen content x. The ferromagnetic impurities evidenced by the field dependence of the high-temperature limiting linewidth are much different in the $x=0.3$ sample. Thus, the ferromagnetic impurities appear to be unimportant in the additional T_2^{-1} relaxation above 170 K.

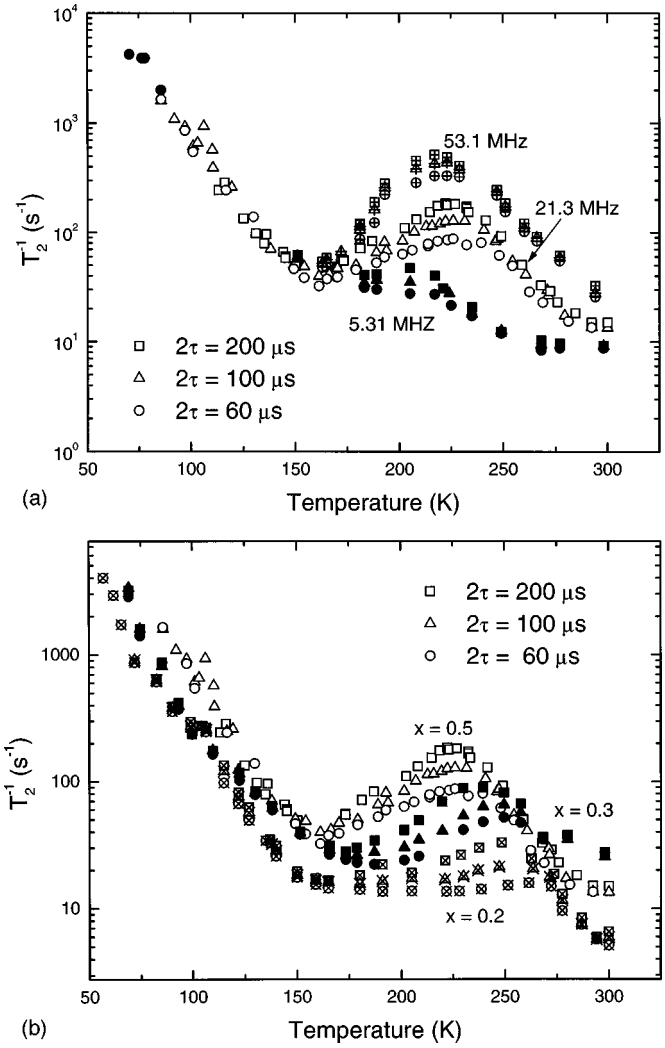

FIG. 3. Dephasing rate T_2^{-1} from CPMG echo trains. Above 170 K, the measured rates are greater than expected from dipolar line narrowing. (a) Data for $x=0.5$ at three resonance frequencies, as marked. The anomalous relaxation increases with field strength. Below the peak, T_2^{-1} depends on the pulse spacing 2τ of the CPMG sequence. (b) Data for three sample compositions x, all at 21.3 MHz. Again, three values of 2τ have been used.

Is the additional relaxation in Figs. 3(a) and 3(b) simply due to diffusion of H atoms through a magnetic-field gradient created by the nonvanishing magnetic susceptibility of the powder particles,[9,16] as discussed in the Introduction? In support of this hypothesis, the additional T_2^{-1} increases with field strength. However, three aspects of the data are inconsistent with this simple and well-known mechanism. First, the data pass through a peak near 225 K; above this temperature, T_2^{-1} again decreases with increasing temperature. For diffusion through internal magnetic-field gradients, one expects the apparent T_2^{-1} to increase with temperature until the H atoms diffuse so rapidly that they can diffuse all the way across a particle in the time T_2. Still faster diffusion would then be described by motional averaging theory. But in $ZrCr_2H_{0.5}$, D is 10^{-7} cm^2/s at 250 K.[3] In a time $t=10^{-2}$ s, the H atom moves an rms displacement along any one axis of $\sqrt{2Dt}$, or 0.45 microns (4500 Å). This is *much* smaller than the 10–50 microns powder size of the samples.

Second, the additional T_2^{-1} relaxation is strongly dependent upon the hydrogen content x, varying nearly a decade near 225 K between $x=0.2$ and 0.5. But the rate of diffusion D measured by pulsed field gradient[22] NMR for $x=0.2$ is only slightly different ($\times 1.3$) than for $x=0.5$ and is actually *larger*.[3] Further, there is no reason to expect large changes in the magnetic susceptibility for such small changes in hydrogen loading (1/15 to 1/6 per metal atom). Indeed, compare $x=0.2$ and 0.5 in Fig. 2(b). Furthermore, the Korringa relaxation constant increases[2] by about a factor of 2 from $x=0.2$ to 0.5, indicating[12] an increase in the Knight shift and electronic spin susceptibility of about 1.4, seemingly too small to result in the strong dependence on x in Fig. 3(b). Thus it is hard to reconcile the large dependence on H content x, evident in Fig. 3(b), with the model of diffusion through field gradients extending across the particles.

Third, all of the T_2^{-1} data in Fig. 3(a) departs from the lower temperature curve at the same temperature (170 K), independent of the field strength and resonance frequency. This is in contrast to the data of $ZrBe_2H_{1.4}$ in Fig. 4 of Ref. 16, where the additional relaxation first becomes evident at a lower temperature at higher field strength. That is, as discussed in the Introduction, the ''peel-off'' temperature (i.e., the temperature where T_2^{-1} first deviates from the lower temperature data) decreases with increasing field. Thus, the field independent peel-off temperature in Fig. 3(a) is inconsistent with the model of diffusion through magnetic-field gradients.

From the fact that all of the data in Fig. 3 peel-off at 170 K, it appears that a subtle transition occurs at 170 K for all three values of x. There is some support for this from the behavior of the diffusion coefficient D, which has a non-Arrhenius temperature dependence.[3] In fact, D shows a marked change in slope (plotted against $1/T$) near 170 K. Indeed, the D data have been empirically fit to a sum of two thermally activated rates, one with a small prefactor and a small activation energy and the other with a large prefactor and a large activation energy. The crossover between the limiting low- and high-temperature behaviors should occur where the two rates are equal. For $x=0.2$ and 0.5, this occurs at 180 and 182 K, respectively. Thus, the D data support the notion of a subtle transition near 170 K.

Is the temperature dependence of the additional dephasing relaxation entirely driven by the temperature dependence of the rate of H-atom diffusion? Recalling the strong dependence of T_2^{-1} upon H concentration x and the near independence of D upon x, we assert the answer to the above question is *no*. The temperature dependence of T_2^{-1} between 250 and 300 K in Fig. 3, when plotted as a function of reciprocal temperature, is well described by an activation temperature (E_a/k_B) of 2900–3300 K. This is much larger than the activation energy of 146–148 meV (1700 K) that best describes the diffusion[3] in the high-temperature region. Thus, the temperature dependence of T_2^{-1} in Fig. 3 must arise from more than just the temperature-dependent rate of diffusion.

What is the significance of the 2τ dependence of the CPMG T_2^{-1} data in Fig. 3? Following Karlicek and Lowe,[23] the π pulses have the effect of multiplying the field shift seen by the spins by -1 at each π pulse. Thus, the field shift is effectively multiplied by a square wave of frequency $1/4\tau$ (in Hz units). The end result is that the rate of dephasing of

the echo train is proportional to the spectral density of the fluctuating field[12] seen by a spin, at the frequency $1/4\tau$ (and, to lesser extents, at the odd harmonics $3/4\tau$, $5/4\tau$, $7/4\tau$, etc.). Thus, the variation of T_2^{-1} with different values of the pulse spacing 2τ reveals the frequency spectrum of the fluctuating fields.

The above view of the dependence of T_2^{-1} on the CPMG pulse spacing is not the view taken in most texts. So it is useful to apply it to a simple problem with a well-known answer. For diffusion in an unbounded region with a uniform magnetic field gradient, we recall that the velocity autocorrelation time is very short so that the power spectrum of particle velocity is constant (flat) across the relevant frequencies. Now position, the time integral of velocity, determines the field in the presence of a uniform gradient; the power spectrum of position will have $1/\omega^2$ character (i.e., $v = i\omega x$ where v and x are velocity and position; *power* spectra involve squares of these quantities). *This* is the reason that the decay rate R varies with the pulse spacing 2τ: from Slichter's text,[12] the decay rate for the CPMG echo train is R,

$$R = \gamma^2 G^2 D \tau^2/3. \tag{2}$$

The well-known τ^2 dependence is from the $1/\omega^2$ spectrum of position fluctuations and the filtering action of the CPMG pulse sequence, resulting in sensitivity to field fluctuations primarily at frequency $1/4\tau$.

Examining the data of Fig. 3(b), one notes that the 2τ dependence of T_2^{-1} is present only on the low-temperature side of the peak [we note that field dependence of T_2^{-1} is present on both sides of the maximum in Fig. 3(a), demonstrating that the same mechanism is at work on both sides]. The sign of the dependence, increasing T_2^{-1} with increasing 2τ, is in accord with Eq. (2) and indicates that the spectral density $J(\omega)$ of the field fluctuations increases with decreasing frequency ω. However, the dependence of T_2^{-1} upon 2τ remains weaker than the $(2\tau)^2$ of Eq. (2). We note the similarity between the present T_2^{-1} data and the behavior of T_1^{-1} near a motional maximum, with frequency dependence appearing only on the low-temperature side of the maximum.[12,24] Furthermore, the temperature of the maximum T_2^{-1} decreases (weakly) with increasing 2τ, again resembling a motional maximum of T_1^{-1} in standard relaxation theory. Thus, these features of the data suggest that the peak in T_2^{-1} occurs when some characteristic frequency associated with the motion passes through frequency $1/4\tau$.

It is useful now to summarize the experimental facts concerning the excess T_2^{-1} relaxation.

1. Above 170 K, the frequency of the spins is being modulated by something other than the dipolar spin-spin interactions. The fluctuations are slow enough that they influence T_2^{-1} but not T_1^{-1}. Further, below ~ 225 K, T_2^{-1} varies with the CPMG pulse spacing 2τ(60–200 μs), indicating that the field fluctuations are not *much* faster than this.

2. The simple model of diffusion of H atoms through field inhomogeneities due to the randomly oriented sample particles cannot explain the peak in T_2^{-1}, the strong dependence on H concentration x, nor the x- and field-independent temperature of the onset of excess transverse relaxation.

3. The field fluctuations govern the excess T_2^{-1} on both sides of the peak. The field fluctuations are stronger at higher fields, as expected if spatially varying susceptibility or Knight shift is involved.

4. The temperature dependence of the excess relaxation is not entirely due to the temperature dependence of H-atom diffusion. Indeed, the onset of excess relaxation at 170 K, independent of x and field, argues for a subtle change in the H subsystem at this temperature. The non-Arrhenius diffusion data support this.

5. The monotonic increase of T_2^{-1} with x suggests that the excess relaxation is intrinsic (not impurity driven) and intimately connected with the H atoms.

It is interesting to note that the anomalous T_2^{-1} enhancement has been observed near the critical point of binary liquid mixtures showing a miscibility gap.[25] In the vicinity of the critical point, long-lived microregions of different chemical composition are known to be formed. Molecular diffusion in such microscopically heterogeneous liquid leads to a time-dependent chemical shift experienced by a nucleus; this results in T_2^{-1} enhancement, as in the case of chemical exchange.[25,26] The magnitude of the T_2^{-1} enhancement depends on three factors: (1) the rate of diffusion, (2) the size of the microregions, and (3) the magnitude of the resonance frequency fluctuations. Estimates for binary liquid mixtures[25] show that the T_2^{-1} enhancement may be observable if the size of the microregions is between 100 and 10 000 Å; for smaller or larger heterogeneous regions the effect is greatly reduced.

The T_2^{-1} anomaly in $ZrCr_2H_x$ can also be explained in terms of low-frequency fluctuations of the proton resonance frequency arising from hydrogen diffusion in a *microscopically inhomogeneous* medium. Presumably, the amplitude and the length scale of the nonuniformity vary with temperature and contribute to the observed temperature dependence of the additional T_2^{-1}. The length scale of the inhomogeneities can be estimated from $\sqrt{2Dt}$, using $t = 100$ μs (from the CPMG pulse spacing 2τ) for the peak near 225 K. The result is about 300 Å; given the absence of a real model for the unusual 2τ dependence, for example, this value is only a gross estimate. Whatever nonuniformity occurs, it appears to influence the proton NMR through changes in the magnetic susceptibility and/or the proton Knight shift.

The microscopic inhomogeneity may be of structural or magnetic origin. In the case of a structural inhomogeneity we expect formation of hydrogen clusters, i.e., phase separation on a microscopic spatial scale. For most metal-hydrogen systems, a uniform solid solution phase transforms with decreasing temperature into a two-phase structure. However, for $ZrCr_2H_x$ with $x \leqslant 0.5$ no signs of *macroscopic* phase separation have been found, at least above 80 K.[1,2,27,28] In this respect the $ZrCr_2H_x$ system resembles the hcp solid solutions α-ScH_x, α-YH_x, and α-LuH_x ($x \lesssim 0.2$), where short-range hydrogen ordering[29–31] provides an alternative to phase separation. In fact, recent heat-capacity[32] and neutron-diffraction[28] measurements are consistent with H(D) ordering in $ZrCr_2H_x(D_x)$ ($x \leqslant 0.7$) that occurs below 100 K. For $ZrCr_2D_{0.7}$ the ordering is found to be long ranged;[28] for lower x a short-range order is likely to exist. It should be noted that the ordering occurs well below the tem-

perature range of the T_2^{-1} anomaly. Therefore the T_2^{-1} enhancement cannot be directly related to the hydrogen ordering. In order to search for a possible phase separation on the scale of about 300 Å, it would be interesting to perform small-angle neutron-scattering measurements in the temperature range 170–230 K.

The other possibility is a formation of some long-period magnetic structure which may be induced by hydrogen. Spin-density waves are known to exist in chromium and some of its alloys.[33] It is not clear whether the presence of Cr in our system is crucial for the observed T_2^{-1} effect. Similar T_2^{-1} anomalous relaxation has been found[34] in the related Laves-phase system $HfCr_2H_x$ with the hexagonal C14 structure.

The NMR evidence provided here for the microscopic inhomogeneity is indirect. Thus, it will be crucial to search for other, more direct evidence such as from x-ray diffraction or from small-angle neutron scattering. We also suggest that the hydrogen diffusion coefficient D measured by the PFG method may be dependent on the time scale of the measurement in the region of spatial inhomogeneity.

IV. CONCLUSIONS

Motion of the H atoms narrows the NMR line in $ZrCr_2H_x$, but inhomogeneous broadening dominates the linewidth above 100 K. The field dependence and sample dependence of the limiting linewidth indicate that both the magnetic susceptibility of the sample and ferromagnetic impurities are the sources of the magnetic broadening.

Additional transverse spin relaxation T_2^{-1} occurs above 170 K. Strong evidence is supplied to exclude the mechanism of diffusion through a gradient arising from the powder particles' susceptibilities. The most pertinent experimental results are summarized in the five numbered items above. The data indicate that the $ZrCr_2H_x$ system becomes spatially modulated above 170 K. A gross estimate of the length scale is 300 Å. Because the NMR evidence for spatial modulation presented here is indirect, we hope that other, more direct techniques will be used to examine this system. Possibilities include x-ray diffraction to examine the Bragg peaks for inhomogeneous broadening, low-angle neutron scattering to reveal inhomogeneity in the H subsystem, and pulsed field gradient NMR measurements of hydrogen diffusion over a range of time scales.

ACKNOWLEDGMENTS

The authors gratefully acknowledge NSF support through Grant No. DMR-9705080. We appreciate informative discussions with R. G. Barnes and R. M. Cotts. The magnet system used here was a generous gift of E. I. DuPont de Nemours and Co. We appreciate magnetization measurements of a sample in the laboratory of J. S. Schilling.

*Present address: Naval Research Laboratory, Chemistry Division, Code 6122, Washington, DC 20375.

†Present address: National Institutes of Health, Bethesda, MD.

[1] A. V. Skripov, M. Yu. Belyaev, and A. P. Stepanov, Solid State Commun. **78**, 909 (1991).

[2] A. V. Skripov and M. Yu. Belyaev, J. Phys.: Condens. Matter **5**, 4767 (1993).

[3] W. Renz, G. Majer, A. V. Skripov, and A. Seeger, J. Phys.: Condens. Matter **6**, 6367 (1994).

[4] R. D. Stoddard and M. S. Conradi, Phys. Rev. B **57**, 10 455 (1998).

[5] A. V. Skripov, M. Pionke, O. Randl, and R. Hempelmann, J. Phys.: Condens. Matter (to be published).

[6] A. V. Skripov, J. C. Cook, D. S. Sibirtsev, C. Karmonik, and R. Hempelmann, J. Phys.: Condens. Matter **10**, 1787 (1998).

[7] R. M. Cotts, Ber. Bunsenges. Phys. Chem. **76**, 760 (1972).

[8] R. G. Barnes, in *Nuclear and Electron Resonance Spectroscopies Applied to Materials Science*, edited by E. N. Kaufmann and G. K. Shenoy, MRS Symposia Proceedings No. 3 (North-Holland, New York, 1981), pp. 19–30.

[9] R. M. Cotts, in Hydrogen in Metals I, edited by G. Alefeld and J. Volkl, Topics in Applied Physics Vol. 28 (Springer-Verlag, New York, 1978), pp. 227–265.

[10] L. E. Drain, Proc. Phys. Soc. London **80**, 1380 (1962).

[11] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

[12] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1990).

[13] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

[14] S. Meiboom and D. Gill, Rev. Sci. Instrum. **29**, 688 (1958).

[15] A. F. Andresen, K. Ontes, and A. J. Maeland, J. Less-Common Met. **89**, 201 (1983).

[16] A. F. McDowell, C. F. Mendelsohn, M. S. Conradi, R. C. Bowman, Jr., and A. J. Maeland, Phys. Rev. B **51**, 6336 (1995).

[17] F. Kimmerle, G. Majer, U. Kaess, A. J. Maeland, M. S. Conradi, and A. F. McDowell, J. Alloys Compd. **264**, 63 (1998).

[18] J. H. Wernick, in *Intermetallic Compounds*, edited by J. H. Westbrook (Wiley, New York, 1967).

[19] G. E. Pake and T. L. Estle, *The Physical Principles of Electron Paramagnetic Resonance* (W. A. Benjamin, Reading, MA, 1973).

[20] P. M. Richards, Phys. Rev. B **36**, 7417 (1987).

[21] R. G. Barnes, J.-W. Han, D. R. Torgeson, D. B. Baker, M. S. Conradi, and R. E. Norberg, Phys. Rev. B **51**, 3503 (1995), and references therein.

[22] E. O. Stejskal and J. E. Tanner, J. Chem. Phys. **42**, 288 (1965).

[23] R. F. Karlicek, Jr. and I. J. Lowe, J. Magn. Reson. **37**, 75 (1980).

[24] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[25] J. E. Anderson, J. Chem. Phys. **50**, 1474 (1969).

[26] J. E. Anderson and K. J. Liu, J. Chem. Phys. **49**, 2850 (1968).

[27] V. A. Somenkov and A. V. Irodova, J. Less-Common Met. **101**, 481 (1984).

[28] P. Fischer, F. Fauth, A. V. Skripov, and V. N. Kozhanov (unpublished).

[29] M. W. McKergow, D. K. Ross, J. E. Bonnet, I. S. Anderson, and O. Schärpf, J. Phys. C **20**, 1909 (1987).

[30] O. Blaschko, J. Pleschiutschnig, P. Vajda, J. P. Burger, and J. N. Daou, Phys. Rev. B **40**, 5344 (1989).

[31] P. Vajda, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, New York, 1995), Vol. 20, pp. 216–221.

[32] A. V. Skripov, A. E. Karkin, and A. V. Mirmelstein, J. Phys.: Condens. Matter **9**, 1191 (1997).

[33] E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).

[34] A. V. Skripov, D. S. Sibirtsev, and A. P. Stepanov (unpublished).