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Journal of Alloys and Compounds 227 (1995) 28–31

Journal of ALLOYS AND COMPOUNDS

Nuclear magnetic resonance study of deuterium diffusion in $ZrCr_2D_x$

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Received 7 December 1994; in final form 6 March 1995

Abstract

Nuclear magnetic resonance measurements of ^2D spin lattice relaxation rates in C15-$ZrCr_2D_x$ ($x = 0.29$, 0.48 and 3.8) and C14-$ZrCr_2D_{4.0}$ have been performed over the temperature range 110–450 K. The experimental results are analysed to obtain the electronic (Korringa) contributions to the relaxation rates and the parameters of deuterium diffusion. For C15-$ZrCr_2D_x$ the deuterium mobility is found to decrease with increasing x. Comparison of the data for $ZrCr_2D_x$ and $ZrCr_2H_x$ shows that in compounds with nearly the same x the hopping rate of D atoms is lower than that of H atoms.

Keywords: Diffusion; Hydrogen in metals; Nuclear magnetic resonance; Isotope effects

1. Introduction

The intermetallic compound $ZrCr_2$ may exist in the form of two structural modifications (the hexagonal C14 or the cubic C15) both of which absorb large amounts of hydrogen. Recent ^1H nuclear magnetic resonance (NMR) experiments [1–3] have revealed the anomalously high hydrogen mobility down to low temperatures in both C14- and C15-$ZrCr_2H_x$ ($x \leqslant 0.5$). Direct measurements of the hydrogen diffusion coefficient D in these compounds by means of pulsed-field-gradient (PFG) NMR [3] have shown that the temperature dependence of D deviates markedly from the Arrhenius behaviour below 200 K. This suggests a change in the dominant diffusion mechanism at low temperatures. In order to understand mechanisms of hydrogen diffusion in these compounds, it is of special importance to study isotope effects in hydrogen motion. In the present work we report the results of ^2D NMR studies of deuterium motion in $ZrCr_2D_x$. The behaviour of ^2D spin lattice relaxation rates in $ZrCr_2D_x$ has been investigated over wide ranges of temperature and deuterium concentration. The results are compared with those derived from ^1H NMR experiments on $ZrCr_2H_x$.

2. Experimental details

The preparation of the starting C14- and C15-type $ZrCr_2$ compounds has been described elsewhere [1]. Small pieces of the host compounds were charged with D_2 gas at a pressure of about 0.3 bar using a Sieverts-type vacuum system, and the deuterium content was determined from the pressure change in the calibrated volume of the system. Measurements were made on powdered samples of C15-$ZrCr_2D_x$ ($x = 0.29$, 0.48 and 3.8) and C14-$ZrCr_2D_{4.0}$. According to the X-ray diffraction analysis, all the studied samples are single-phase solid solutions retaining the host metal structure (C15 or C14) of the corresponding deuterium-free materials. The lattice parameters of the studied samples are listed in Table 1.

NMR measurements were performed on a Bruker SXP pulse spectrometer. The ^2D spin lattice relaxation rates T_1^{-1} were measured at the frequency $\omega/2\pi = 13.8$ MHz using the conventional inversion–recovery method. In all cases the recovery could be fitted by an exponential function.

3. Results and discussion

The results of the ^2D spin lattice relaxation rate measurements are presented in Figs. 1 and 2. For all the samples studied the relaxation rate shows a characteristic maximum associated with deuterium motion. This maximum is observed at the temperature T_{max} at which $\omega\tau_d \approx 1$, τ_d being the mean dwell time of a D atom in an interstitial site. It can be seen that for C15-type compounds the value of T_{max} considerably increases with increasing x. This means that the deuterium mobility strongly decreases with increasing D con-

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SSDI 0925-8388(95)01631-7

Table 1
Lattice parameters, electronic contributions to ^{2}D spin lattice relaxation rate and parameters of deuterium diffusion estimated from the experimental data

Sample	Lattice parameters		$(T_{1e}T)^{-1}$ (s^{-1} K^{-1})	$\bar{E}_a$ (eV)	ΔE_a (eV)	ν_0 (s^{-1})
	a (Å)	c (Å)				
C15-$ZrCr_2D_{0.29}$	7.259	–	1.4×10^{-4}	0.18	0.08	5.6×10^{12}
C15-$ZrCr_2D_{0.48}$	7.282	–	2.6×10^{-4}	0.16	0.06	1.0×10^{12}
C15-$ZrCr_2D_{3.8}$	7.715	–	6.0×10^{-3}	0.22		
C14-$ZrCr_2D_{4.0}$	5.448	8.840	4.5×10^{-3}	0.24		

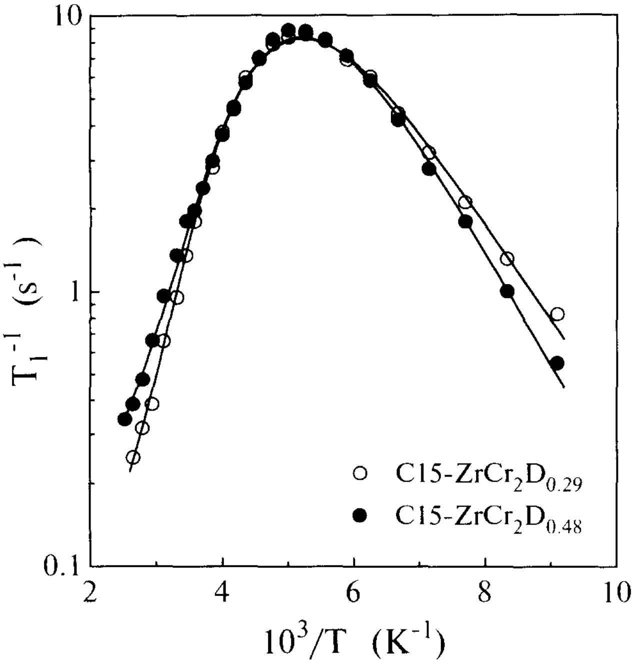

Fig. 1. Temperature dependence of the ^{2}D spin lattice relaxation rate in C15-$ZrCr_2D_{0.29}$ and C15-$ZrCr_2D_{0.48}$ measured at 13.8 MHz. The lines represent the fit of the BPP model with a gaussian distribution of E_a to the data.

tent. Similar concentration dependence of H mobility has been observed for C15-$ZrCr_2H_x$ [1–3].

The measured ^{2}D spin lattice relaxation rate in metal–deuterium systems usually results from the sum of three main contributions:

$$T_1^{-1} = T_{1e}^{-1} + T_{1d}^{-1} + T_{1Q}^{-1} \qquad (1)$$

where T_{1e}^{-1} is the contribution due to the hyperfine interactions with conduction electrons, T_d^{-1} is the contribution due to internuclear dipole–dipole interactions modulated by D motion, and T_{1Q} originates from the interaction of nuclear quadrupole moments with the local electric field gradients (EFGs) modulated by D motion. Since the local symmetry of interstitial sites occupied by D in C14- and C15-type compounds is non-cubic, EFG on ^{2}D is produced mainly by the neighbouring metal atoms. As can be seen from Figs. 1 and 2, the maximum value of the relaxation rate is nearly the same for all the samples studied. This indicates that the motional contributions to the ^{2}D relaxation rate are dominated by T_{1Q}^{-1}, since T_{1d}^{-1} should depend strongly on D concentration. The quadrupole contribution T_{1Q}^{-1} is expected to have the same temperature dependence as the dipolar deuterium–metal contribution [4,5].

The electronic contribution T_{1e}^{-1} is typically proportional to temperature. This term appears to be small for the low x $ZrCr_2D_x$ in the temperature range of our measurements. However, for the high x samples (C15-$ZrCr_2D_{3.8}$ and C14-$ZrCr_2D_{4.0}$) the electronic contribution is important, as can be seen from the upward curvature of the data at $T \geqslant 280$ K (Fig. 2). The strong increase in the electronic relaxation rate with increasing x has been previously found for the proton T_1^{-1} in $ZrCr_2H_x$ [1]. Such a behaviour suggests that the density of electron states at the Fermi level increases significantly with increasing hydrogen content. The values of T_{1e}^{-1} estimated at 400 K are 2.4 s^{-1} and 1.8 s^{-1} for C15-$ZrCr_2D_{3.8}$ and C14-$ZrCr_2D_{4.0}$ respectively. These values can be compared to those obtained by scaling the proton T_{1e}^{-1} data for $ZrCr_2H_x$

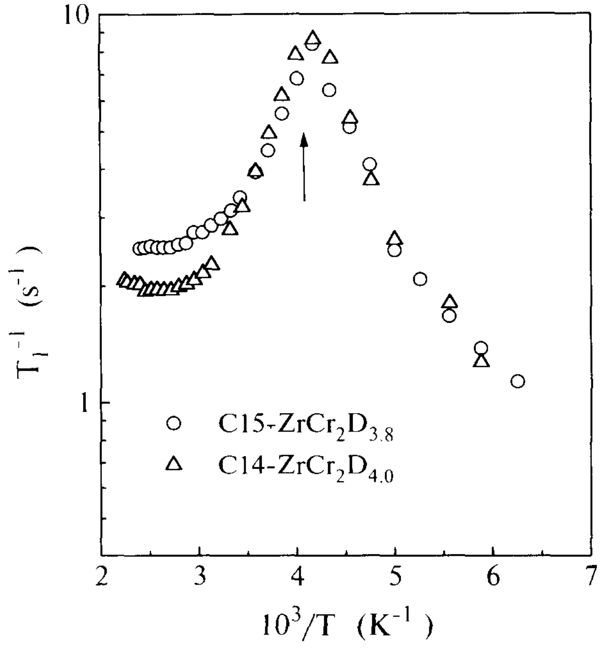

Fig. 2. Temperature dependence of the ^{2}D spin lattice relaxation rate in C15-$ZrCr_2D_{3.8}$ and C14-$ZrCr_2D_{4.0}$ measured at 13.8 MHz. The arrow shows the phase transition temperature for C15-$ZrCr_2D_{3.8}$. For C14-$ZrC_2D_{4.0}$ the phase change occurs near the same temperature, the transition region being somewhat broadened.

with $(\gamma_D/\gamma_H)^2$, where $\gamma_{D(H)}$ is the gyromagnetic ratio of ^{2}D (^{1}H). The corresponding scaled T_{1e}^{-1} values at 400 K are 1.6 s^{-1} for C15-$ZrCr_2H_{3.3}$ [1] and 1.9 s^{-1} for C14-$ZrCr_2H_{4.2}$ [6].

The temperature dependence of the motional contribution to the ^{2}D relaxation rate in the low x $ZrCr_2D_x$ can be satisfactorily described by the Bloembergen–Purcell–Pound (BPP) model with a gaussian distribution of activation energies E_a for D motion (Fig. 1). A similar model has been found to give a good description of the proton relaxation data in low x $ZrCr_2H_x$ [2]. Parameters resulting from the fit for C15-$ZrCr_2D_{0.29}$ and C15-$ZrCr_2D_{0.48}$ are listed in Table 1. These include the average activation energy $\bar{E}_a$, the distribution width at half-maximum ΔE_a, the attempt frequency ν_0 and the electronic contribution $(T_{1e}T)^{-1}$. It should be noted that such a model may overestimate the value of ΔE_a, since it does not take into account the possibility of changes in the average activation energy with temperature. In fact, recent measurements of D in low x $ZrCr_2H_x$ by PFG NMR [3] have revealed pronounced deviations from the Arrhenius behaviour below 200 K. However, the values of $\bar{E}_a$ are expected to provide a basis for comparing different systems, since $\bar{E}_a$ should determine the behaviour of both D and $T_{1d,1Q}^{-1}$ at high temperatures [7]. The values of $\bar{E}_a$ for D in low x $ZrCr_2D_x$ are higher than those for H in low x $ZrCr_2H_x$, as derived from both the proton relaxation rate [2] and PFG NMR [3] measurements. For example, the high-temperature values of the activation energy for the long-range H diffusion in C15-$ZrCr_2H_{0.3}$ and C15-$ZrCr_2H_{0.5}$ are 0.141 eV and 0.137 eV respectively [3]. Thus $\bar{E}_a^D \geqslant \bar{E}_a^H$ for C15-$ZrCr_2H_x(D_x)$ with low x. The same inequality has been found for the related C15-$ZrV_2H_x(D_x)$ system in the low x region [8] and for binary metal–hydrogen systems with b.c.c. host metal structure [9]. Such an inequality results in slower motion of D atoms, as compared with that of H atoms, at low temperatures. This is consistent with the fact that T_{max} values for ^{2}D in C15-ZrC_2D_x ($x=0.29$ and 0.48) are higher than those for ^{1}H in C15-$ZrCr_2H_x$ [1,2] with nearly the same x. It should be noted, however, that in our case a direct comparison of the attempt frequencies for hydrides and deuterides is hardly possible [4] since the dominant motional relaxation mechanisms for ^{1}H and ^{2}D are different (dipole–dipole and quadrupole respectively). At present we can only state that our results on isotope effects do not contradict the adiabatic mechanism of quantum diffusion suggested for low x $ZrCr_2H_x$ at $T \geqslant 200$ K [3].

The high x samples (C15-$ZrCr_2D_{3.8}$ and C14-$ZrCr_2D_{4.0}$) exhibit phase transitions related to deuterium ordering [10,11] near 250 K. Therefore a continuous fit of the relaxation rate data for these samples in the entire temperature range studied would make no physical sense. In fact, as can be seen from Fig. 2, the relaxation rate maximum for C15-$ZrCr_2D_{3.8}$ is 'folded'. This means that the maximum is much sharper than that predicted by the BPP model with the Arrhenius temperature dependence of τ_d, since τ_d is expected to change rapidly near the transition point. Similar 'folding' of the T_1^{-1} maxima has been earlier observed for $ZrV_2H_4(D_4)$ and $HfV_2H_4(D_4)$ near the order–disorder phase transition [8]. The electronic contributions $(T_{1e}T)^{-1}$ and the activation energies estimated from the high-temperature slope of the relaxation rate curves for C15-$ZrCr_2D_{3.8}$ and C14-$ZrCr_2D_{4.0}$ are included in Table 1. The difference between motional parameters of D in C14- and C15-type compounds appears to be small. As in the case of the low x compounds, the relaxation rate maximum in high x $ZrCr_2D_x$ is shifted to higher temperatures with respect to that in $ZrCr_2H_x$ with nearly the same x [1]. This suggests that the hopping rate of D atoms is lower than that of H atoms in the temperature range of our measurements.

4. Conclusions

The main results of our measurements of ^{2}D spin lattice relaxation rates in C15-$ZrCr_2D_x$ ($x=0.29$, 0.48 and 3.8) and C14-$ZrCr_2D_{4.0}$ may be summarized as follows.

The electronic contribution to the ^{2}D relaxation rate in C15-$ZrCr_2D_x$ is found to increase strongly with increasing x. A similar trend has been earlier observed for the proton T_{1e}^{-1} in $ZrCr_2H_x$. These results suggest that the density of electron states at the Fermi level in $ZrCr_2H_x(D_x)$ increases significantly with increasing hydrogen content.

For low x $ZrCr_2D_x$ the temperature dependence of the motional contribution to the ^{2}D relaxation rate can be reasonably described in terms of the BPP model with a gaussian distribution of activation energies. The resulting average activation energies for D diffusion in $ZrCr_2D_x$ are lower than those for H diffusion in $ZrCr_2H_x$. For high x $ZrCr_2D_x$ the temperature dependence of the relaxation rate is affected by the order–disorder phase transition. For both high and low x samples the hopping rate of D atoms is lower than that of H atoms in the temperature range of our measurements.

Acknowledgments

We are grateful to M.Yu. Belyaev for assistance in NMR experiments at initial stages of this work and to L.N. Padurets for preparation of the high x deuterides. The research described in this paper was made possible in part by a grant from the International Science Foundation. A.V.S. also acknowledges financial support of the Alexander von Humboldt Foundation.

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