NUCLEAR MAGNETIC RESONANCE STUDY OF HYDROGEN MOBILITY IN $HfCr_2H_x(D_x)$ COMPOUNDS WITH A *C*14-TYPE STRUCTURE

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Introduction

The investigation of physical properties of hydrided Laves phases attracts great attention in the last years, which appears to be primarily due to the large variety of phase transitions and the unusual dynamics of hydrogen atoms in these systems. Information on the diffusion of hydrogen in Laves phases was generalized in the review [1]. For cubic Laves phases (structure of the *C*15 type), the microscopic picture of motion of hydrogen atoms and the systematics of diffusion phenomena are well understood. One of the most interesting features of hydrogen diffusion in these systems is the coexistence of two types of hydrogen-atom jumps with different characteristic frequencies [1]. For hexagonal Laves phases (structure of the *C*14 type), there exists only fragmentary information on hydrogen diffusion (in systems $ZrCr_2H_x$ [2]). This work is aimed at the investigation of hydrogen diffusion in the $HfCr_2$ compound with a *C*14-type structure, as well as of the effect of isotope substitution H↔D on the diffusion parameters. To obtain microscopic information on the motion of H and D atoms, we have measured spin-lattice relaxation times T_1 of ^{1}H and ^{2}D nuclei.

Results and discussion

The $HfCr_2$ compound was prepared by arc melting of the components in a helium atmosphere. According to X-ray diffraction, the intermetallic compound obtained is single-phase and has a crystal structure of the *C*14 type with the lattice parameters a = 5.067 Å, c = 8.259 Å. The hydrogenation of the samples from the gas phase was performed in a vacuum apparatus of the Sieverts type. Measurements were carried out on powder samples of $HfCr_2H_x$ and $HfCr_2D_y$, x=0.3; 0.6; 0.74; y=0.28; 0.64.

The results of the measurements of spin-lattice relaxation rates T_1^{-1} for the ^{1}H и ^{2}D nuclei in $HfCr_2H_{0.6}$ and $HfCr_2D_y$ are shown in Figs. 1 and 2.

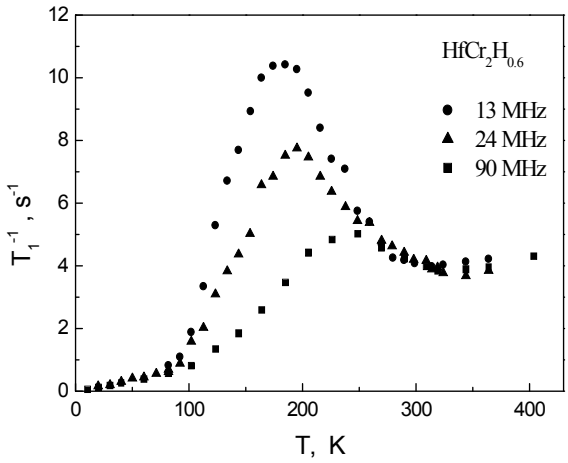

Fig. 1. Temperature dependence of the spin-lattice relaxation rate of protons in $HfCr_2H_{0.6}$ at the frequencies of 13, 24 and 90 MHz.

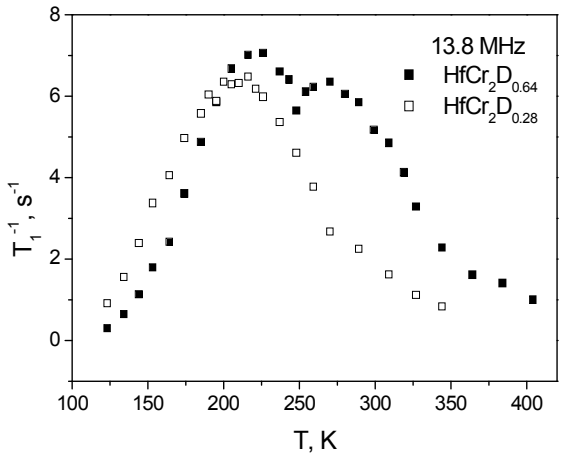

Fig. 2. Temperature dependence of the spin-lattice relaxation rate of ^{2}D in $HfCr_2D_{0.28}$ and $HfCr_2D_{0.64}$ at the frequency of 13.8 MHz.

The spin-lattice relaxation rate in metal-hydrogen systems is usually determined by the sum of two main contributions: $T_1^{-1} = T_{1e}^{-1} + T_{1m}^{-1}$, where T_{1e}^{-1} is the contribution related to the hyperfine interaction of nuclei with conduction

electrons, and T_{1m}^{-1} is the contribution due to the modulation of nuclear dipole-dipole interaction (and quadrupole interaction for nuclei with spin $I > 1/2$) by atomic motion. The T_{1m}^{-1} contribution related to atomic motion exhibits a resonance-frequency-dependent maximum. This maximum arises at a temperature at which the atomic jump rate $\tau_d^{-1}(T)$ becomes approximately equal to the frequency of the nuclear magnetic resonance (NMR).

To estimate the parameters of H(D) motion, we have to separate the contributions T_{1e}^{-1} and T_{1m}^{-1} to the measured spin-lattice relaxation rate. The electron contribution T_{1e}^{-1} can be measured directly in the range of low temperatures. Indeed, at $T \leq 40$ K the experimental $T_1^{-1}(T)$ dependences for protons in $HfCr_2H_x$ are well described by a linear function C_eT. The temperature dependences of T_{1m}^{-1} for ^1H и ^2D were determined by subtracting the electron contributions $T_{1e}^{-1}(T)$ from the experimental data for $T_1^{-1}(T)$. Figure 3 shows the behavior of T_{1m}^{-1} in $HfCr_2H_{0.3}$ and $HfCr_2D_{0.28}$ as a function of the reciprocal temperature.

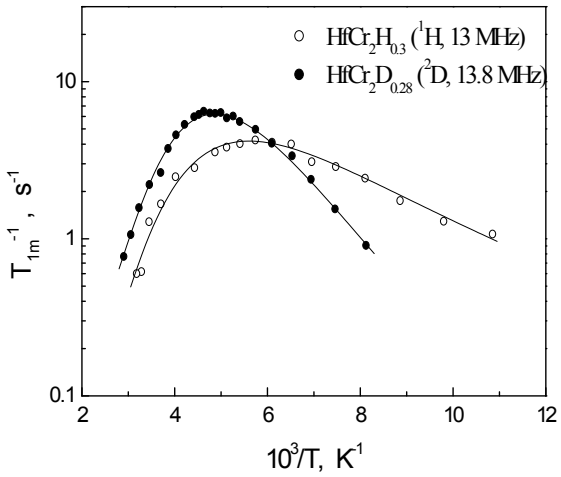

Fig. 3. The motional contributions to the spin-lattice relaxation rate of ^1H and ^2D in $HfCr_2H_{0.3}$ and $HfCr_2D_{0.28}$ as functions of the reciprocal temperature. Solid lines show the results of approximation using the BBP model with a Gaussian distribution of activation energies.

For parametrization of the experimental data on T_{1m}^{-1} in $HfCr_2H_x$ and $HfCr_2D_{0.28}$ we have used the Bloembergen-Pursell-Pound (BPP) model with a Gaussian distribution of activation energies. The parameters of the model are the average value of the activation energy $\overline{E}_a$, the width of the distribution (dispersion) ΔE_a, and the pre-exponentional factor τ_{d0}^{-1}. The results of such a simulation for the samples with $x \approx 0.3$ are shown by solid lines in Fig. 3. The values of the parameters obtained for $HfCr_2H_x$ and $HfCr_2D_{0.28}$ are represented in the table.

Sample	τ_{d0}^{-1}, s^{-1}	$\overline{E}_a$, eV	ΔE_a, eV
$HfCr_2H_{0.3}$	1.1×10^{12}	0.138	0.043
$HfCr_2H_{0.6}$	1.2×10^{12}	0.147	0.032
$HfCr_2H_{0.74}$	4.3×10^{11}	0.141	0.025
$HfCr_2D_{0.28}$	1.2×10^{12}	0.155	0.029

A comparison of the results for the hydrided and deuterided samples of close compositions shows that the magnitude of the pre-exponentional factor τ_{d0}^{-1} is almost independent of the isotope, and the following inequality is valid for the average values of the activation energy: $\overline{E}_a^H < \overline{E}_a^D$. An increase in the concentration of H in $HfCr_2$ leads to a slight increment in $\overline{E}_a$.

For the $HfCr_2D_{0.64}$ compound, the temperature dependence of T_1^{-1} differs from those found for the other samples studied in this work. The $T_1^{-1}(T)$ dependence for $HfCr_2D_{0.64}$ can be represented as a superposition of two overlapping peaks (Fig. 2). This feature is likely to result from a non-uniform distribution of deuterium concentration over the sample volume. For the hydrided samples of $HfCr_2H_x$ such a concentration non-uniformity manifests itself only at $x > 1.3$.

Conclusions

Measurements of the spin-lattice relaxation rate of ^1H and ^2D in the hydrided (deuterided) compounds $HfCr_2H_x$ and $HfCr_2D_y$ with a *C*14-type structure show that the diffusion mobility of H (D) in these systems remains high down to low temperatures. At $T \approx 200$ K, the diffusion mobility of hydrogen in $HfCr_2$ is higher than in other intermetallic compounds studied, except for $ZrCr_2$. An increase in the concentration of H (D) in $HfCr_2$ leads to a decrease in the jump rate of hydrogen atoms. A comparison of the data for the hydrided and deuterided compounds shows that, at equal temperatures, the jump rate of D atoms is lower than that of H atoms.

References

1. Skripov AV. Hydrogen diffusion in Laves-phase compounds. Defect and Diffusion Forum. 2004; 224-225: 75-92.
2. Skripov AV, Belyaev MYu, Stepanov A.P. NMR study of hydrogen mobility in C14- and C15-type compounds $ZrCr_2H_x$. Solid State Commun. 1991; 78 (10): 909-912.