Isotope effect in a Cu–H(D) system with hexagonal hydride phase

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Abstract

The decomposition pressure p_{dec} of copper deuteride has been experimentally determined in a diamond anvil cell. The value of 6.8 ± 0.6 GPa is lower than the corresponding pressure of copper hydride. The difference between standard Gibbs energies of decomposition of copper hydride and deuteride has been calculated as equal to -5.2 kJ mol^{-1} (H$_2$). The zero-point energy of hydrogen vibration in the hydride lattice has been obtained applying the localized harmonic oscillator model.
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1. Introduction

The direct manifestation of differences in the properties of hydrogen isotopes interacting with metal is the value of the pressures of formation and decomposition of corresponding solid phases. An experimentally observed isotope effect can be explained, at least qualitatively, within the localized harmonic oscillator model [1], where the main and only parameter used is the zero-point energy of hydrogen vibration in the metal lattice, $h\nu_H$. Furthermore, extended treatment, which takes into account additional terms associated with non-vibrational contributions to the chemical potential of hydrogen in the solid phase, could also be applied [2]. The zero-point energy calculated from the model could be compared with that obtained experimentally from inelastic neutron scattering (INS), infrared or Raman absorption measurements. Most of the papers concerning the isotope effect in metal–hydrogen systems are related to typical metallic hydrides in regions of relatively low hydrogen pressure. Therefore, it would be interesting to check the reliability of such a simple model in the case of high-pressure metal hydrides and systems with a non-metallic type of metal–hydrogen bonding.

From the point of view of the character of the metal–hydrogen bond, a copper–hydrogen (deuterium) system with a hexagonal hydride (deuteride) phase fits well to the purpose mentioned above. It is usually referred to as a covalent hydride [3,4]. Most studies concerning this system have focused on copper hydride (CuH), whereas there has been limited information about the deuteride. Goedkoop and Andresen [5] confirmed the wurtzite structure of both phases using X-ray and neutron diffraction techniques. Warf and Feitknecht [6] reported the lattice parameter, $a = 2.93 \pm 0.03$ Å and $c = 4.68 \pm 0.05$ Å for copper deuteride.

This paper reports experimental results on the decomposition pressure of copper deuteride. The values of decomposition pressure of the hydride [7] and the deuteride are compared and the $h\nu_H$ value is evaluated.

2. Experimental

Copper deuteride was synthesized according to the procedure successfully applied for obtaining the hydride phase [6]. The obvious difference was that deuterated reagents (water and hypophosphorous acid) were used. The precipitated product was analyzed by mass spectrometric (Hiden Analytical Instrument) and X-ray diffraction methods. In order to avoid decomposition of the copper deuteride, samples after synthesis were kept in the Dewar vessel with dry ice. It has been proved that in such conditions copper hydride or deuteride can be stored over the year without noticeable

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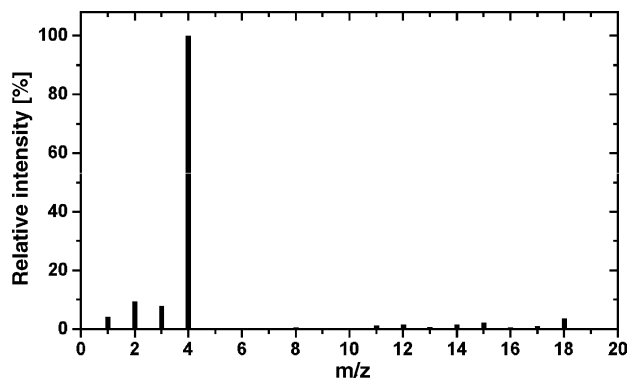 *E-mail address:* temar@ichf.edu.pl (M. Tkacz).

Fig. 1. Relative intensity of mass spectrometry signals for the atomic mass up to 20.

decomposition. Furthermore, the samples obtained in the way described above have shown relatively good stability even at room temperature. This allows for the loading of a diamond anvil cell without using low temperature facilities. The result of mass spectrometry analysis of the gas desorbed during thermal decomposition of the sample is presented in Fig. 1.

For the determination of deuterium and hydrogen concentration in the samples, the signals on masses 4 and 2 which correspond to D_2^+ and H_2^+ species, being proportional to the partial pressures of D_2 and H_2, were compared with the reference assuming the same ionization potentials of both isotopes.

The atomic ratio of deuterium to hydrogen in the samples was about 10 as can be estimated from Fig. 1 by the signals ratio on masses 4 and 2. The atomic ratio $H + D/Cu$ was about 0.8. The X-ray diffraction pattern of copper deuteride (Fig. 2) clearly shows the hexagonal structure of copper atoms in the deuteride lattice with parameters $a = 2.88$ $c = 4.58$ nearly the same as for copper hydride [7].

High-pressure experiments were performed using a diamond anvil cell (DAC). The sample was loaded into a hole 0.2 mm in diameter made in a rhenium gasket. The DAC was cooled down to $-50\,^\circ\text{C}$ to avoid pressure-induced decomposition of copper deuteride. Next, high pressure was gener-
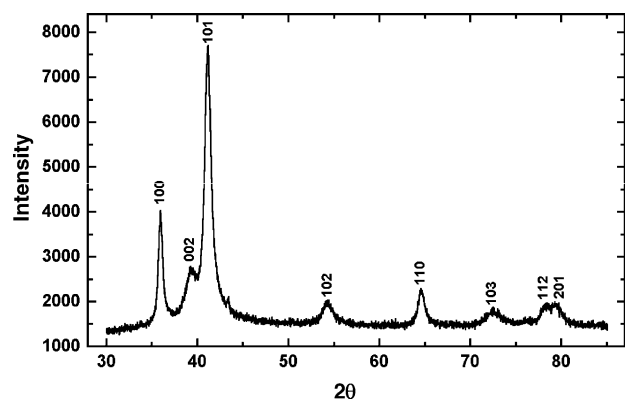

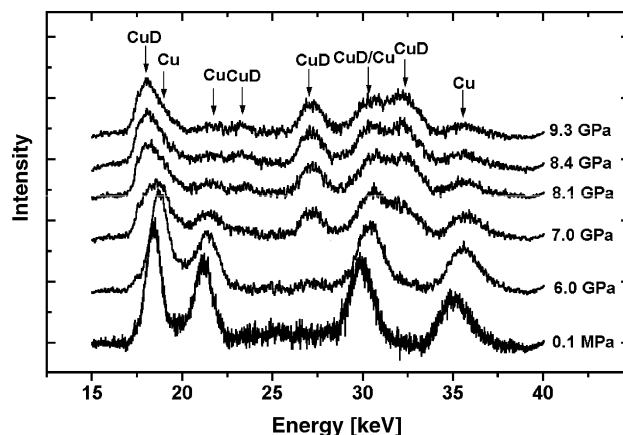Fig. 2. X-ray diffraction pattern of copper deuteride.

Fig. 3. EDXRD spectra of the copper sample at different pressures.

ated and the DAC was allowed to warm up slowly to room temperature. At high pressure, in the absence of deuterium, copper deuteride was found to be partly decomposed. In this way deuterium pressure was spontaneously created inside the hole. This allows the deuteride itself to be used as a source of D_2 gas. Then the pressure was gradually reduced and the phase composition of the sample was monitored at each step by the energy dispersive X-ray diffraction method (EDXRD). The pressure was determined by the ruby fluorescence technique. Except for the first stage when sample was warmed up from low temperature, all experimental procedures were carried out at room temperature including diffraction and pressure measurements.

3. Results

The set of diffraction patterns collected at different pressures and after background subtraction is presented in Fig. 3.

Due to the partial decomposition of copper deuteride during the loading procedure, even at the highest pressures the diffraction patterns indicate the presence of pure copper. The relative intensities of the selected diffraction lines have been used to estimate the phase composition of the sample. The same procedure has been successfully employed to determine the pressure of decomposition of copper hydride, as published recently [7]. It could be noticed that copper deuteride starts to decompose at about 7.0 GPa and the decomposition process is completed at about 6.0 GPa. The pressure of decomposition of copper deuteride was estimated at 6.8 ± 0.6 GPa. The intensities of the deuteride lines remain remarkably constant at the highest pressures, suggesting the stability region for the compound.

4. Discussion

The equation used to calculate the oscillator energy from equilibrium pressure measurements is essentially the same as

that usually applied for a solid solution [1]:

$$RT \ln \frac{f_D}{f_H} - \int_{0.1\,MPa}^{p_H} V_H \, dp - \int_{0.1\,MPa}^{p_D} V_D \, dp$$

$$= 3RT \ln \left(\frac{1 - \exp^{-h\nu_H / \sqrt{2}kT}}{1 - \exp^{-h\nu_H / kT}} \right) - 0.4349 R \frac{h\nu_H}{k}$$

$$- \frac{1}{2}[(\mu_{D_2}^0 - U_{D_2}^0) - (\mu_{H_2}^0 - U_{H_2}^0)] + \frac{1}{2}(D_{D_2} - D_{H_2})$$

$$(1)$$

where p_H, p_D, f_H, f_D are equilibrium pressure and corresponding fugacity for hydride and deuteride, $\mu_{H_2}^0$, $\mu_{D_2}^0$ are standard chemical potentials of hydrogen (deuterium) in gas the phase, $U_{H_2}^0$, $U_{D_2}^0$ are energies of hydrogen and deuterium molecules including zero-point energy at 0 K, D_{H_2}, D_{D_2} are dissociation energies of hydrogen and deuterium molecules, V_H, V_D are partial volumes of a hydrogen and deuterium atoms in the solid phase, k is the Boltzman constant, and T is temperature.

An additional term describing the pressure dependence of the partial volume of hydrogen (deuterium) in the solid phase was added in order to take into account the influence of pressure on the chemical potential of hydrogen (deuterium) atoms. The partial volume of hydrogen (deuterium) was defined as the difference between the molar volume of the hydride (deuteride) and copper. The compressibility of the hydride [8] and deuteride was assumed to be the same. The thermodynamic values of hydrogen gas as well as the pressure–fugacity relation can be found in available literature.

The value of $h\nu_H$ calculated according to Eq. (1) for the copper–hydrogen system with a hexagonal hydride phase is equal to about 200 meV.

Ross et al. [9] showed that the zero-point energy of a hydrogen atom vibrating in a tetrahedral site could be described by the function:

$$h\nu_H = A R^{-1.5} \qquad (2)$$

where A is a constant equal to 414, R is metal–hydrogen distance.

In a copper hydride lattice hydrogen atoms are located in distorted tetrahedral interstitial sites, where the distance between the hydrogen and copper atom along the c direction is shorter than the three others (1.72 Å and 1.76 Å, respectively). For the sake of simplicity, we assumed that the tetrahedron is ideal with all distances equal to 1.75 Å. Then, according to Eq. (2), for copper hydride $h\nu_H = 180$ meV. This result is in agreement with the value obtained from high-pressure studies. Additional confirmation of this finding could be extracted from studies of the photon absorption of copper hydride in an infrared region. Unfortunately, the majority of attempts to obtain infrared spectra of solid hydride have been unsuccessful [10,11]. The only positive result has been reported by Samodelov [12]. The author observed an absorption line at 208 meV for samples synthesized both by chemical (in an aqueous solution) and electrochemical methods. Golovanova et al. [11] measured the spectra of a pyridine complex of copper hydride isolated as the product of synthesis of copper hydride in an organic medium. The authors ascribed absorption peak observed at 205 meV to longitudinal copper–hydrogen vibration. These results strongly support the value presented in this paper.

In Eq. (1), the left-hand side in fact corresponds to the difference of the standard Gibbs energy of decomposition of stoichiometric copper hydride and deuteride. The calculated value of $\Delta(\Delta G^0)$ is equal to -5.2 kJ mol^{-1} (H$_2$), being very similar to the value for the molybdenum–hydrogen (deuterium) system [13], which, like the Cu–H(D) system, is characterized by a high value of decomposition pressure of the hydride and deuteride phase.

It is also possible to offer a hypothesis regarding the nature of the metal–hydrogen bond in copper hydride. The halides of monovalent copper are definitely ionic compounds. At room temperature they possess a zinc blend crystal structure, and at high temperature transform into a wurtzite-type structure like that of copper hydride. The surrounding of the atoms is essentially the same in both types of structure and there should not be any significant difference in the hydrogen atom vibration energy in the zinc blende or wutrzite-type lattice. Therefore, the value of $h\nu_H$ for ionic hexagonal copper hydride could be estimated from the data on the vibration energy of the copper–halide bond. The frequency of longitudinal vibrations in CuCl, CuBr and CuJ [14] is proportional to the reciprocal of the square root of reduced mass. Following this dependence the $h\nu_H$ of fully ionic hexagonal CuH should be equal to 128 meV, which is remarkably smaller than the value calculated from the decomposition pressure measurements. This energy corresponds to the Cu–H distance of 2.18 Å according to the relation presented by Ross et al. [9]. It is far from 1.75 Å in copper hydride synthesized in an aqueous solution and is much closer to 2.08 Å predicted for ionic CuH by Warf [4]. This clearly indicates that the metal–hydrogen bond in copper hydride is essentially covalent.

5. Conclusion

The decomposition pressure of copper deuteride has been experimentally determined for the first time. On the basis of these experimental data, the zero-point energy of hydrogen vibration was calculated applying the localized harmonic oscillator model. The result is in good agreement with the value predicted by the empirical relation on the vibration energy of hydrogen in a tetrahedral interstitial site. The difference of the standard Gibbs energy for the decomposition process of copper hydride and deuteride has been calculated.

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