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HIGH TEMPERATURE INVESTIGATION OF THE DYNAMICS AND THE THERMODYNAMICS OF ZrH–U SYSTEM BY NEUTRON SCATTERING

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1. Introduction

Metal-hydrogen systems present a high fundamental and applied interest.

Among these systems combinations of Zr with H were extensively investigated so far mainly due to their applicability as nuclear materials. The structural and dynamic features as well as the thermodynamic properties of Zr-H(D) systems seem to be very well known since long time. At room temperature within the composition range Zr to ZrH_2 there are a solid solution of H in α-Zr with HCP metal sublattice and several hydrides phases, δ-hydride with FCC metal sublattice, γ-hydride with FCO metal sublattice and ε-hydride with FCT metal sublattice [1,2]. Vibrational properties [2-9] as well as thermodynamic and transport functions [10-16] have been investigated by a variety of experimental techniques including INS, X-ray scattering, calorimetric or dilatometric techniques, termal or electrical measurements.

More recently, a new interest led to intense study of these systems when their superconductivity was found [17]. Superconducting transition temperatures T_C are strongly enhanced (3.14 K for Zr-H and 4.65 K for Zr-D) compared with those of pure metal (0.7 K). A lot of studies have been devoted to microscopic properties investigations trying to explain this phenomenon based on a strong coupling between high-frequency or hypotetical low-frequency H(D) vibrations to the electronic system. INS was one of the most used techniques [5,8] and very recently, low-frequency H vibrations, firstly theoretical predicted [18] have been experimentally revealed in Zr [19,20]. New results with higher resolution have been obtained from recent INS measurements at DIN-2PI spectrometer, IBR-2 pulsed reactor of JINR-Dubna [21] and at NEAT spectrometer, BER II reactor of BENSC-Berlin [22].

However, a microscopic investigation of the changes on the vibrational and thermodynamic properties according to different spatial distributions of Zr atoms at transition from pure metal to stoichiometric hydride or deuteride has been only recently performed [23]. Also, an accurate investigation of the evolution of microscopic properties in the range of high temperatures and the correlation with changes in macroscopic properties have not been completely performed up to now. The evaluation of thermodynamic functions by several independent methods is particulary desirable for a complex solid system. By measuring the GVDS of a system one can provide information regarding the temperature dependence of its thermophysical properties.

We extend here an experimental study started few years ago by inelastic neutron scattering investigation on different Zr and Zr based hydrides and deuterides, performing now measurements of vibrational frequencies of δ Zr hydride containing uranium, $ZrH_{1.6}U_{0.32}$, in the range of high

temperatures, between 293 and 973 K. Starting from the basic properties of H in Zr studied in terms of GVDS, the influences of microscopic features on thermophysical properties have been derived.

2. Theoretical background

2.1 Inelastic neutron scattering

The double differential scattering cross section for neutrons can be written as the sum of a coherent part and an incoherent part,

$$d^2\sigma / d\Omega dE = \left(d^2\sigma / d\Omega dE\right)_{coh} + \left(d^2\sigma / d\Omega dE\right)_{inc} \quad (1)$$

The experimental information obtained from a neutron scattering process on metal-hydrogen systems is essentially determinated by:

(i) the very large incoherent scattering cross section of proton, $\sigma_{inc} >> \sigma_{coh}$ and about 10-20 times larger than that of other elements, and

(ii) the small H mass.

Under these circumstances the slow neutrons "see" practically only the H and, because the scattering intensity varies in proportion to the square of vibration amplitude, i.e. inversely as the mass, the amplitude of H components in the spectrum is relatively large. The scattering due to the host metal lattice is more or less negligible excepting the case of low hydrogen content. Dealing with the incoherent cross section in the case of H atoms forming a simple cubic Bravais lattice it can be written

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc} = \left(\frac{\sigma}{4\pi}\right)\left(\frac{k}{k_0}\right) S_{inc}(Q,\omega) \quad (2)$$

where $S_{inc}(Q,\omega)$ is the incoherent scattering function. The conservation of momentum and energy during the scattering yield

$$\hbar\vec{Q} = \hbar\left(\vec{k}_0 - \vec{k}\right) \qquad \hbar\omega = \varepsilon = E_0 - E \quad (3)$$

where E_0, E, $\vec{k}_0$ and $\vec{k}$ are neutron energy and wave vector before and after scattering and $\vec{Q}$ is the scattering vector. In a harmonic one-phonon approximation one obtains

$$S_{inc}(Q,\omega) = \left(\frac{\hbar\, F(\hbar\omega / k_B T)}{2M|\omega|}\right) Q^2\, g(\omega)\, exp(-2W) \quad (4)$$

with g(ω) the GVDS and F(x) the thermal population factor given by $F(x)=(e^x-1)^{-1} + 1/2\ (1\pm1)$ with the upper and lower sign corresponding to phonon creation and phonon annihilation, respectively.

The Debye-Waller factor exp(-2W) is defined usually by $exp(-Q^2\langle u^2\rangle)$ where $\langle u^2\rangle$ is the mean-square amplitude of the proton. If $Q^2\langle u^2\rangle$ is sufficiently small (≤ 0.1, that means Q generally between 2÷4 A^{-1}) the one-phonon processes dominate. Otherwise, the multiphonon contribution becomes important. Optic modes in metal hydrides are characterized by energies typical in the range $\hbar\omega_H = 0.1 \ldots 0.2$ eV. Consequently, $k >> k_0$ so that

$$Q^2 = (k_0 - k)^2 \cong k^2 = 2m\omega_H / \hbar^2 \qquad (5)$$

It follows that Q values occur between 7÷10 A^{-1} and the probability for multiphonon processes becomes rather high. Their contribution can be estimated from the phonon expansion of the symmetric incoherent scattering law described by

$$\tilde{S}(Q,\omega) = exp(-2W)\sum_{n=0}^{\infty}\frac{(2W)^n}{n!}G_n(\omega) \qquad (6)$$

where

$$G_n(\omega) = \int_{-\infty}^{\infty} G_1(\omega-\omega')\,G_{n-1}(\omega')\,d\omega' \qquad (7)$$

with

$$G_1(\omega) = \frac{g(\omega)}{2\omega\gamma(0)sinh(\hbar\omega / 2k_BT)} \quad \text{and} \quad \gamma(0) = \int_0^{\infty}\frac{g(\omega)}{\omega}coth(\hbar\omega / 2k_BT)\,d\omega \qquad (8)$$

Here, the frequency distribution g(ω) should to fulfil the normalization condition $\int g(\omega)d\omega = 1$.

Generally, H atoms do not form a Bravais lattice so that eq. (4) can be considered as a definition of an apparent frequency spectrum if M is considered as the H mass for the optic part of the experimental spectrum and as the metal atom mass in the case of the acoustic one.

2.2 Thermodynamic functions

For a metal-hydrogen compound presenting both acoustic and optical vibrations clearly independent each other the specific heat C_V is defined by

$$C_P = (C_P - C_V) + \gamma T + F(T) + 4E(u_0) + 2E(u_1) \qquad (9)$$

where γT, F(T) and $E(u_i)$ are the electronic, acoustic modes and Einstein (optical modes) contributions to the specific heat. The latter is defined for one degree of freedom as

$$E(u_i) = R\,u_i^2\ exp(u_i)\left(exp(u_i)-1\right)^{-2} \quad \text{with } u_i = \hbar\omega_i / k_BT \qquad (10)$$

If the optical modes are three time degenerated, presenting the same energy $\hbar\omega_E$ (as is assumed by the classical Einstein model of the specific heat), a new parameter θ_E, called Einstein temperature can be introduced by

$$\hbar\omega_E = k_B\theta_E \tag{11}$$

so that Einstein contribution to the specific heat can be done also by

$$C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2 \frac{exp(\theta_E/T)}{(exp(\theta_E/T)-1)^2} \tag{12}$$

The acoustic modes contribution can be calculated using

$$C_V = Nk_B\int_0^{\infty}\frac{exp(\hbar\omega/k_BT)}{(exp(\hbar\omega/k_BT)-1)^2}\left(\frac{\hbar\omega}{k_BT}\right)^2 g(\omega)d\omega \tag{13}$$

where $g(\omega)$ is the acoustic part of GVDS. If the classical Debye model is applied to describe the acoustic vibrations also a new parameter can be introduced, θ_D, called the Debye temperature and related to the high frequency limit of lattice vibrations through

$$\hbar\omega_{max} = k_B\theta_D \tag{14}$$

The lattice contribution to the specific heat can also be written as

$$C_V^{ac} = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^n exp(x)}{(exp(x)-1)^2}dx \tag{15}$$

In eqns. (12), (13) and (15) the number of unit cells of the sample N is related to the themodynamic constant R through $sk_BN=R$, where s is the number of atoms in the unit cell.

3. Experimental

The experimental investigations have been performed by inelastic slow neutron scattering using the DIN-2PI direct geometry time-of-flight spectrometer set-up at IBR-2 pulsed reactor of JINR Dubna [24]. The measurements with a resolution of 0.5 meV (full width at half maximum of the elastic scattering taken on a vanadium sample) were taken using a monochromatic neutron beam of 10 meV obtained by means of a curved slits chopper rotating at a constant phase against pulses given by the reactor.

The investigations have been performed at different temperatures above the room one, covering the range this system is used as fuel-moderator ensemble in TRIGA reactors: 293, 378, 578, 773 and 973 K. After all typical corrections have been applyied, the time-of-flight experimental data have been converted in $d^2\sigma/d\Omega dE$ and then, using the one-phonon approximation given by eq.(4), in GVDS, further used for microscopic and macroscopic properties analysis.

4. Data analysis and discussion

Experimental data obtained in terms of GVDS have been firstly analysed in order to separate the one-phonon contribution to the multiphononic one, the latter becoming very important with the increasing of temperature. Using an iterative procedure based on the formalism presented by eqns. (6-8) the multiphononic spectra have been calculated and so, a clear separation between the acoustic range specific to lattice vibrations and the optical one specific to H vibrations has been obtained.

Figs. 1 and 2 present the acoustic part of GVDS for two temperatures, 293 K and 973 K. In the last case the large contribution of the multiphononic contribution is clear observed.

The one-phonon spectrum of the acoustic part of GVDS for all investigated temperatures higher than the room one is presented in Fig. 3.

From the separate analysis of the acoustic and the optical parts of GVDS the high frequency limit of lattice vibrations, $\hbar\omega_{max}$ and the frequency of H optical vibrations, $\hbar\omega_H$ have been obtained as functions of temperature. From this analysis the specific Debye and Einstein temperatures depending on temperature, $\theta_D(T)$ and $\theta_E(T)$ have been obtained (Fig. 4). It is important to underline that optical modes move toward lower energies with increasing of temperature, from 148 meV at room tempearture to 135 meV at 973K. Also, for higher temperatures optical H vibrations have been observed up to the third order harmonics (Fig. 5), informations about H potential in Zr in the presence of U atoms beeing obtained.

As it can be observed from the Fig. 6, presenting the higher harmonics of optical H vibrations, for the second harmonics $\hbar\omega_{II}$ an energy shift of its position from the harmonic value $2\hbar\omega_I$=270 meV was detected. This shift is about 7 meV and also some anharmonic details have been revealed at small energies. Also the third harmonics is shifted from its harmonic value. From an analysis in terms of [5] considering a small anharmonic potential disturbance of the form c_4x^4, the n^{th} vibration level ε_n relative to the ground state can be written as $\varepsilon_n=\hbar\omega_0 n+\beta(n^2+n)$, n=1,2,3... where $\beta = 3\hbar^2 c_4 / 2m_H^2\omega_0^2$, m_H the H mass and ω_0 the harmonic frequency. The anharmonicity parameter β allowed to derive a potential of a "well-type" similar with that for δ-$ZrH_{1.6}$ earlier measured [25].

Taking into account the correlation between microscopic and macroscopic functions of a solid system (eqns. 10, 13) and the temperature dependence of GVDS the specific heat at constant volume, C_V, has been obtained.

The specific heat at constant pressure, C_P, has been estimated with approximation, using a similar procedure as for pure Zr [26]. In the harmonic approximation C_P can be calculated through

Table I Temperature dependence of the acoustic and optical energy excitations and of the thermodynamic quantitites obtained from INS data measured on $ZrH_{1.6}U_{0.32}$ at different temperatures

T [K]	$\hbar\omega^{ac}_{max}$ [meV]	$\hbar\omega^{opt}$ [meV]	C_v^{ac} [cal/mol K]	C_v^{opt} [cal/mol K]	C_p^{calc} [cal/mol K]	θ_D [K]	θ_E [K]
293	38	148	5.649	1.171		441.86	1720.9
378	41.86	145	5.704	2.824	6.855 (ac)	486.74	1686
578	42.7	141	5.889	6.387		496.51	1639.5
773	43.34	138	5.913	8.481		503.95	1604.7
973	44.5	136	5.956	9.674		517.44	1581.4

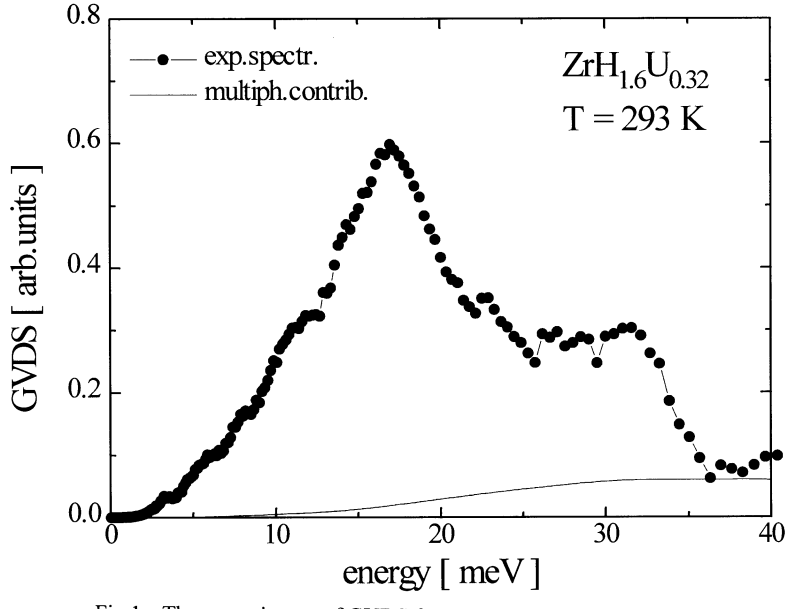

Fig.1 The acoustic part of GVDS for $ZrH_{1.6}U_{0.32}$ at room temperature

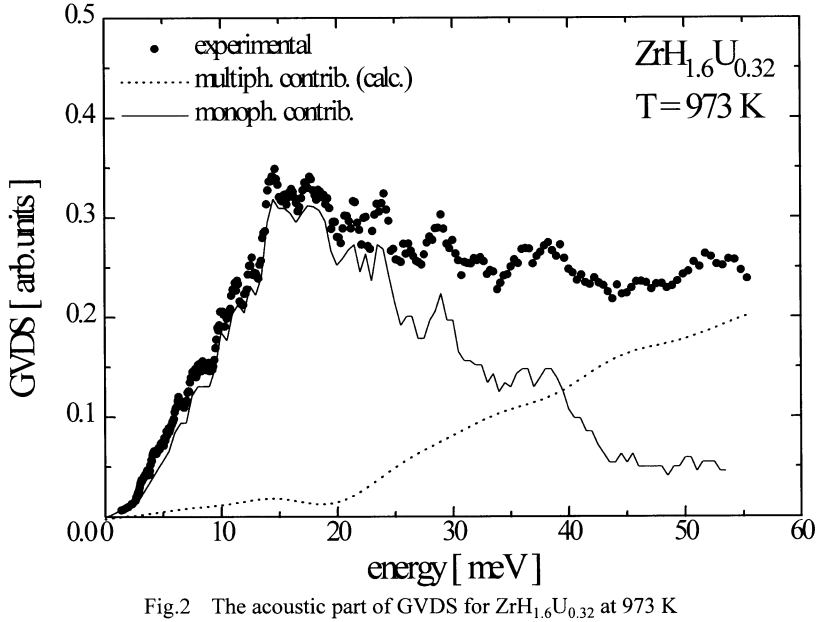

Fig.2 The acoustic part of GVDS for $ZrH_{1.6}U_{0.32}$ at 973 K

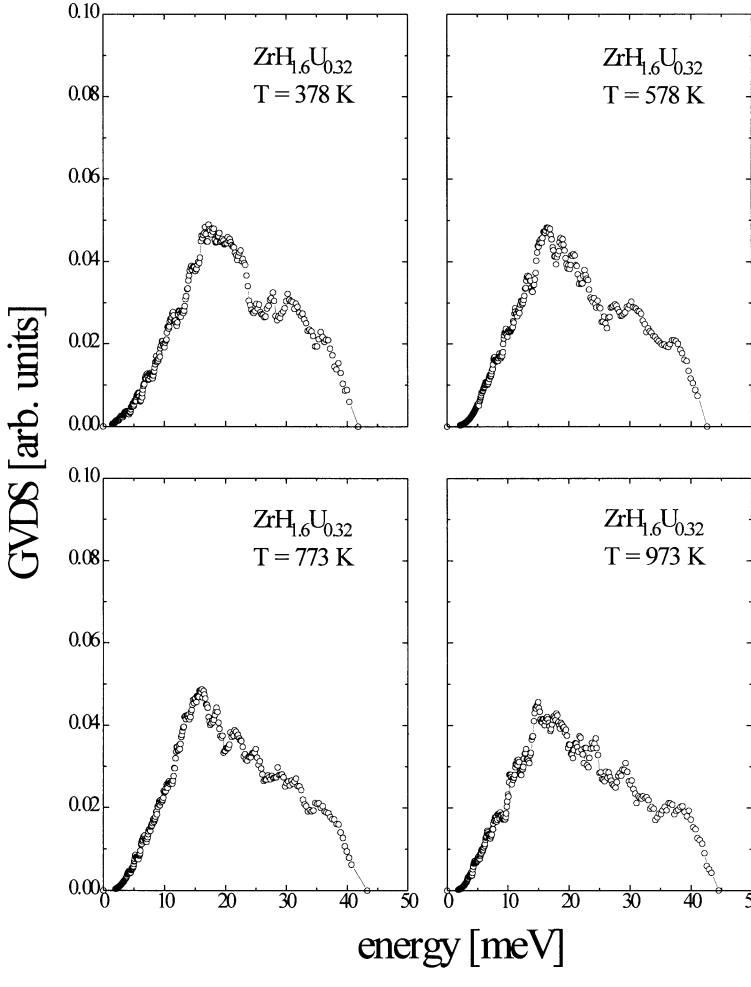

Fig.3 Temperature dependence of the monophononic contribution in the acoustic part of GVDS

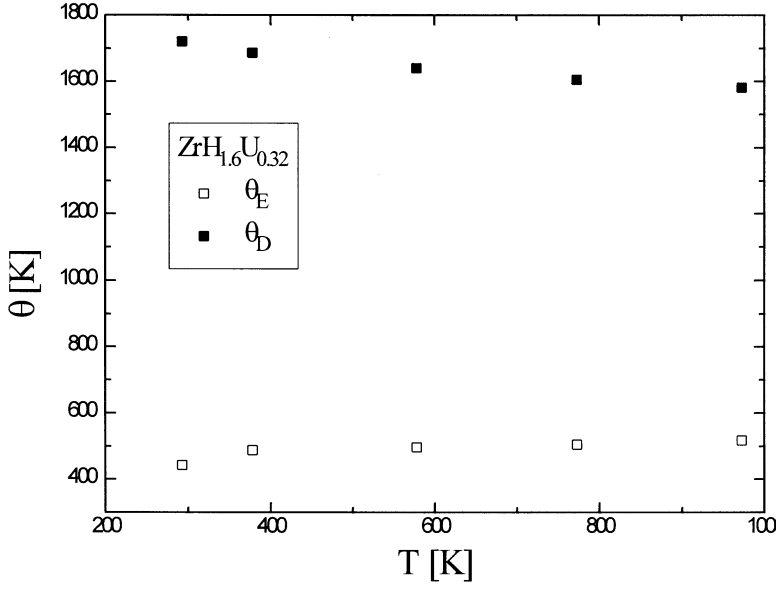

Fig.4 Temperature dependence of the specific Debye and Einstein temperatures for $ZrH_{1.6}U_{0.32}$

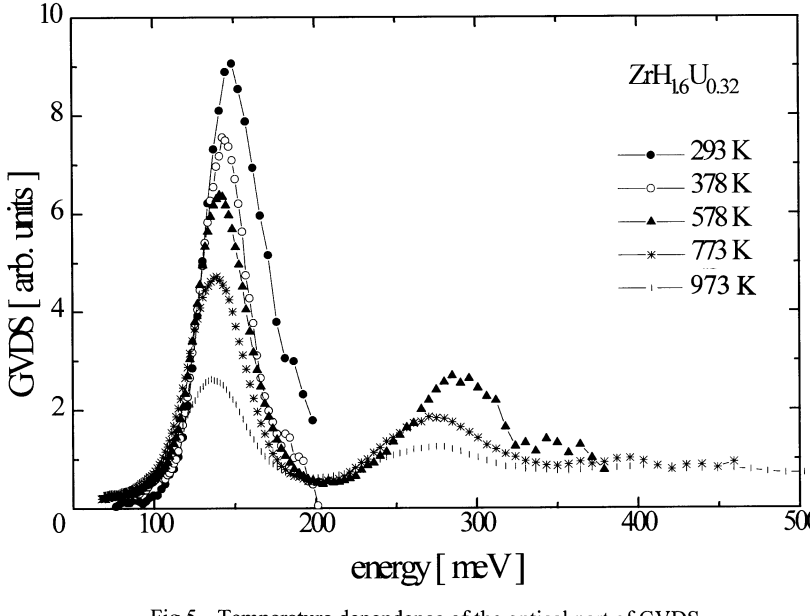

Fig.5 Temperature dependence of the optical part of GVDS

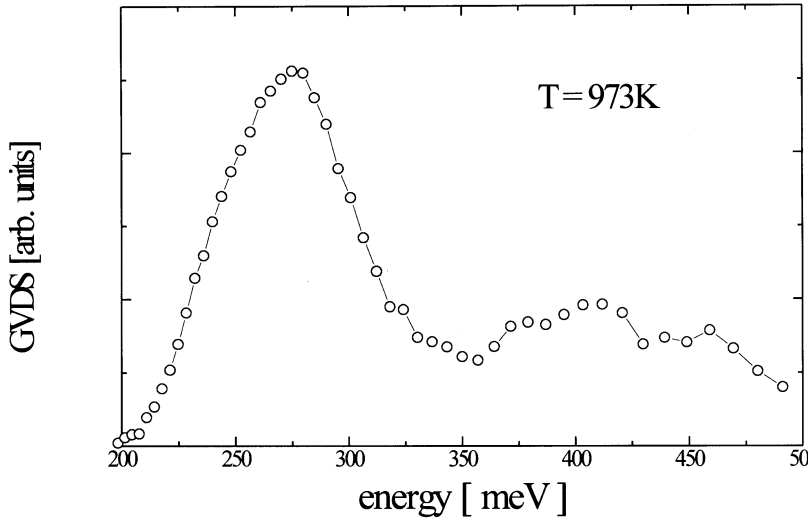

Fig.6 Higher harmonics of H vibrations observed at 973 K

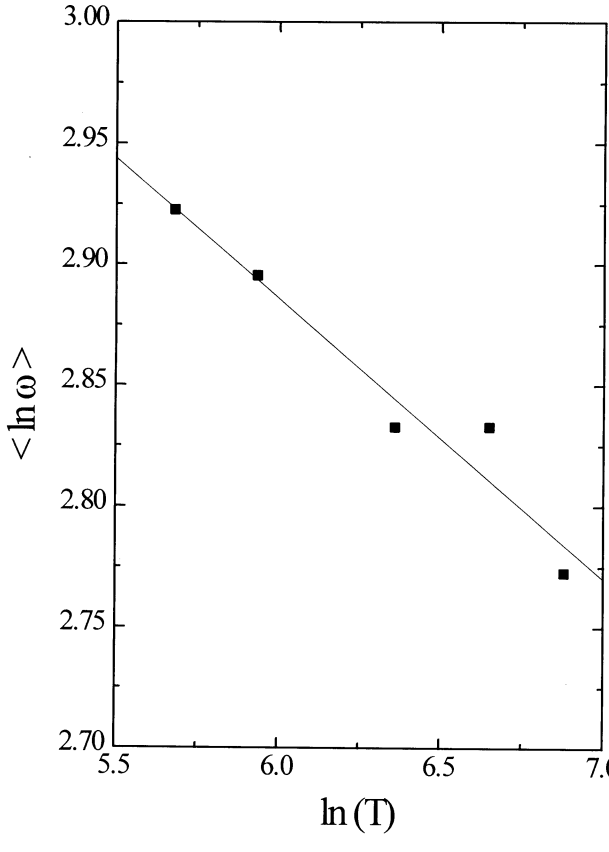

Fig.7 Temperature dependence of <ln ω>

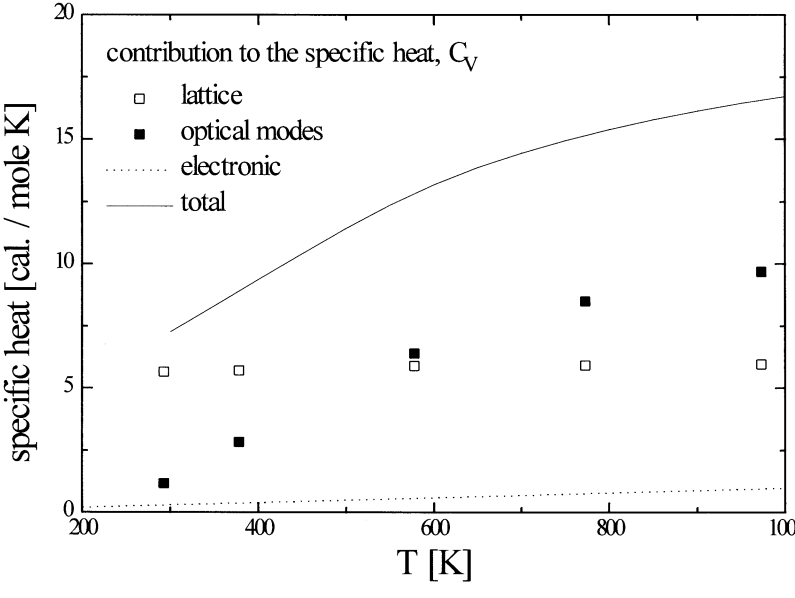

Fig.8 Total specific heat C_V of $ZrH_{1.6}U_{0.32}$ evaluated from microscopic data

$$C_P = Nk_B \sum_{\sigma} \frac{x_\sigma^2}{sinh^2(x_\sigma)} \left[1 - \left(\frac{\partial ln(\omega_\sigma)}{\partial ln T} \right)_P \right] \quad (16)$$

where $x_\sigma = (\hbar\omega_\sigma)/2k_BT$, σ being related to different phonon branches. The first term represents the quasiharmonic contribution, $C_P(QH)$ while the second one becomes from the GVDS temperature dependence. In the case of high temperatures, according to $x_\sigma << 1$,

$$C_P \approx 3Nk_B \left[1 - \left(\frac{\partial < ln\omega >}{\partial ln T} \right)_P \right] \quad (17)$$

where

$$< ln\omega >= \int g(\omega, T) ln\, \omega \; d\omega \quad (18)$$

The function <ln ω> calculated from the above formula is shown in Fig. 7.

All thermodynamic functions calculated from microscopic data expressed in terms of GVDS are presented in Table I.

Fig. 8 presents the total specific heat of $ZrH_{1.6}U_{0.32}$ calculated using eq. (9) as a function of temperature. The electronic contribution has been roughly approximated tacking for γ the same value as for $ZrH_{1.6}$, $\gamma = 9.8 \times 10^{-4}$ cal/mole x K^2.

5. Conclusions

The vibrational spectrum for $ZrH_{1.6}U_{0.32}$ has been measured at different temperatures, between 293 and 973 K by INS. An accurate analysis of experimental data allowed to obtain the temperature dependence of its microscopic properties. H optical vibrations observed up to third order harmonics allowed to get some informations about H potential. Different thermodynamics functions are derived from the correlation between microscopic and macroscopic properties.

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Пэдуреану И. и др. E14-2000-120
Высокотемпературные исследования динамики
и термодинамики ZrH–U-систем с помощью рассеяния нейтронов

С помощью неупругого рассеяния нейтронов проведены измерения частотных спектров в δ–Zr-гидриде, содержащем уран ($ZrH_{1,6}U_{0,32}$), при высоких температурах от 293 до 973 К на спектрометре ДИН-2ПИ на реакторе ИБР-2. Раздельный анализ акустической и оптической областей частотного спектра позволил установить температурную зависимость высокочастотного предела колебаний решетки и оптических колебаний и получить информацию о потенциале водорода в решетке циркония при наличии атомов урана. Исходя из основных свойств термодинамических функций получены характеристические температуры Дебая (Θ_D) и Эйнштейна (Θ_E), вычислена полная теплоемкость при измеренных температурах.

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High Temperature Investigation of the Dynamics
and the Thermodynamics of ZrH–U System by Neutron Scattering

Inelastic neutron scattering (INS) measurements of the vabrational frequencies in δ–Zr hydride containing uranium, $ZrH_{1.6}U_{0.32}$, have been performed in the range of high temperatures, between 293 and 973 K, at DIN-2PI time-of-flight spectrometer, IBR-2 pulsed reactor of JINR-Dubna. From the temperature dependence of the generalized vibrational density of states (GVDS), information about the H potential have been obtained and also high frequency limit of the lattice vibrations and frequency of optical vabrations have been studied as functions of temperature. Starting from the basic properties, the main thermodynamic functions, the characteristic Debye and Einstein temperatures and the total specific heat have been derived.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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