High Pressure Neutron Studies to 25 GPa: Some Recent Results

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We review some results recently obtained using the Paris-Edinburgh cell for high pressure neutron studies up to 25 GPa, both structural and lattice dynamical studies: Low temperature (85 K) structural studies on recovered D₂O ice VIII in the pressure range 0-7 GPa, experiments to 23 GPa to resolve the high pressure structure of YbD₂, and inelastic neutron scattering experiments on single crystalline Ge and Zn to study their transverse acoustic phonon frequencies to 10 GPa.

[neutron diffraction, inelastic neutron scattering, Paris-Edinburgh cell]

1. Introduction

The recent development of the large volume Paris-Edinburgh (PE) cell has had a major impact on high pressure neutron scattering. Initially this breakthrough was confined to time-of-flight neutron diffraction on powder samples but, as a result of further technique developments, has now been extended to inelastic neutron scattering on single crystals using triple-axis spectrometers. In this contribution we report on only a few recent results for both subjects. They will, at the same time, reflect the experimental possibilities using this device on pulsed (spallation) and reactor sources. Results on other subjects will be reported in separate contributions to the Proceedings, such as on high-pressure structural studies of hydroxides and molecular ices (Loveday et al.), on ice VII and ice VIII to 20 GPa (Nelmes et al.) and on magnetic studies of iron sulfide under pressure (Marshall et al.).

2. Results and Discussion

In recent experiments on D₂O at ISIS, the UK pulsed source, we have investigated the behaviour of phase VIII at low temperatures [1]. Ice VIII crystallizes in a tetragonal structure as shown in Fig. 1 and consists of two interpenetrating D₂O sublattices containing molecules with the dipole moments pointing parallel and antiparallel to the c-axis, respectively. Below 125 K, this phase can be quenched to ambient pressure, and the corresponding solid was believed to be identical to D₂O VIII [2]. However, the extrapolation to zero pressure of the phonon and vibron modes measured above 2 GPa [3] does not coincide with the frequencies observed in metastable ice VIII, indicating significant structural changes in the pressure range 0-2 GPa at low temperatures. Measurements in this P-T domain require gaseous helium to drive the piston of the Paris-Edinburgh cell equipped with a Bridgman unsupported area seal as described in ref. [4]. In a first experiment, the equation of state (EOS) of D₂O VIII was determined at 85 K for pressures up to 4 GPa using a mixture of D₂O and lead powder. The EOS of Pb is known at 300 K and values for 85 K may be obtained using Vinet's method [5]. The experimental values for (V/V₀)(P) of D₂O VIII obtained in this way are identical within 0.2% to those published previously [6]. The EOS of recovered D₂O VIII is hence

completely regular and identical within experimental error with the one expected on the basis of the data of unrecovered samples. In a second experiment, the structural pressure dependence was measured on a pure sample of D₂O VIII at 85 K. Diffraction patterns were collected for 26 pressures in the range 0-7 GPa, for several loadings, both on the upstroke and downstroke. Rietveld analysis revealed an anomalous change in the oxygen atomic coordinate $z(O)$ as shown in Fig. 2. At high density the value of $z(O)$ is shown to reach a pressure-independent value of 0.1102, whereas it is constant below 1 GPa at 0.1070. Between, $z(O)$ varies strongly nonlinear, a behaviour which is also seen in the tetragonal distortion parameter $\epsilon = 2c[1/8 - z(O)]$, see Fig. 2. This value, which represents the distance between the two interpenetrating D₂O sublattices of ice VIII, shows a 20% increase between 4 and 0 GPa. This behaviour indicates hence a weakening of the internetwork bonds which hold together the two D₂O networks of the ice VIII structure. This finding explains discrepancies found between the low-temperature vibrational frequencies of ice VIII at high pressure and those of quenched samples.

Fig. 1. The structure of D₂O VIII. Large spheres represent oxygen atoms and small spheres deuterium atoms. The separation ϵ between the two sublattices is marked.

Fig. 2. (a) Fractional coordinates $z(O)$ and (b) tetragonal distortion parameter ϵ of D_2O VIII at 85 K. The dashed curves shown are guides to the eye. The dotted line represent the extrapolated high pressure behaviour of $z(O)$ and ϵ from this work and Ref. [7].

As an example for structural studies at very high pressure we report some preliminary results of experiments on ytterbium dihydride (YbH_2 , YbD_2). This systems undergoes a first-order phase transition at ~ 16 GPa which may be driven by a valence instability of the Yb ion. The high pressure phase was studied by EDX up to 60 GPa [8] and indexed as a distorted hcp structure, but the positions of the hydrogen atoms remained unknown. Due to the strong scattering of Yb for x-rays, the lack of single crystal samples and the elevated pressures necessary to study this phase, neutron powder scattering using the PE cell is the only available technique to solve this problem. High pressure data on YbD_2 up to 23 GPa were collected recently on the new PEARL high-pressure station at ISIS. Such elevated pressures require the use of sintered diamond anvils as described in ref. [9]. The available sample volume in such a set-up is $< 30 \text{ mm}^3$ which is, however, sufficient to obtain refineable spectra within a few hours of data collection time. The orthorhombic (Pnma) low pressure structure was studied including the pressure dependence of the six refineable fractional atomic coordinates up to 16 GPa. Data were collected in the region where both phases are present allowing an accurate determination of the volume change. Figure 3 shows a spectrum of YbD_2 in the high pressure phase at 23 GPa after $\sim 8 \text{ h}$ (1575 μAh) of collection time. Preliminary data analysis reveals the deuterium atoms to be located on a double hexagonal sublattice, as previously suggested by Lebech et al. [10]. Figure 3 shows the fit including the difference curve assuming such a structure (space group $P6_3/mmc$). The powder sample suffered from strong preferred orientation and the Rietveld analysis had to

model this. The hydrogen arrangement seems to be unique among the many structures in which metal hydrides occur. The structural sequence in YbD_2 is identical with the one found in BaF_2 , which crystallizes above 3 GPa in the same orthorhombic Pnma phase (cotunnite) and transforms to the $P6_3/mmc$ structure beyond 12 GPa [11].

Fig. 3. A spectrum collected from YbD_2 at 23 GPa at the PEARL station of the ISIS spallation source (U.K.). The line through the data points represents a fit assuming a $P6_3/mmc$ structure suggested in ref. [10]. Note that there are contaminant reflections of the sintered diamond anvils.

Inelastic neutron scattering using the PE cell has started after the development of the techniques required to compress single crystals up to 10 GPa [12]. We were particularly interested in the study of phonon dispersion curves, and the 2T1 triple-axis spectrometer located at the ORPHEE reactor at the Laboratoire de Léon Brillouin at Saclay (France) provides sufficient flux for such measurements.

The dispersion curves of transverse acoustic phonons of the tetrahedrally bonded semiconductors (Si, Ge, GaAs, ZnTe, etc.) show characteristic features, which have been extensively studied in the past [13]. These modes show negative Grüneisen parameters $\gamma_j(q) = -\partial \ln \omega_j(q) / \partial \ln V$ (j : mode, q : wave vector, ω : frequency, V : volume) at zone boundary points X and L, as revealed by two-phonon Raman studies. The behaviour of the phonon frequencies away from high symmetry points of the Brillouin zone has, however, remained unknown, as well as the analytical form of their pressure dependences.

We have reinvestigated the pressure dependence of the TA phonon modes of tetrahedrally bonded semiconductors by inelastic neutron scattering to 9.7 GPa [14,15]. Germanium was chosen due to its favourable neutron scattering properties, but the results obtained in our experiments should apply to many other systems of this family. Disc-shaped single crystals of 25 mm^3 volume were compressed with the Paris-Edinburgh cell using to a set-up described previously [15]. Lead was used as the pressure-transmitting medium and the pressures were

determined by the measured change in lattice parameters and Murnaghan's equation of state with $B=74.37$ GPa and $B'=4.76$ [16]. Recording times for one scan were between 1 and 7 hours, depending on the phonon and the pressure. Raw data of various constant Q-scans can be found in refs. [14,15]. Figure 4 shows the pressure induced frequency shift in terms of mode Grüneisen parameters, along with other experimental data presently available.

Fig. 4. Mode Grüneisen parameters $\gamma_i(q) = -\partial \ln \omega_i(q) / \partial \ln V$ of germanium. The dots and circles are derived from measured frequency shifts to ~ 5 GPa and 2.3 GPa, respectively.

For small wave vectors our results agree reasonably well with ultrasonic measurements [17] and the value of $\gamma_{TA}(X)$ is in good agreement with published Raman data [18]. In contrast, the decrease of the TA(L) frequency is at least twice as large as indicated by previous tunneling spectroscopy measurements [19]. The phonon frequencies soften under pressure in a large part of the Brillouin zone, see Figure 4. In addition, we observe a nonlinear pressure dependence for all wave vectors studied in these measurements. These nonlinearities lead to a decrease of most frequencies at high pressures - even those which showed initially positive values of $\gamma_i(q)$. Figure 4 also includes results of recent *ab initio* calculation by density functional perturbation theory [14,15]. They represent the so far most ambitious and most successful attempt to calculate the pressure dependence of phonon frequencies. We find excellent agreement between theory and experiment, for all wave vectors and all modes. These calculations also provide data on the pressure dependence of the optical mode of Ge which fit to less than 1% with recent measurements of Ulrich et al [20]. The joint experimental and theoretical approach has also allowed us to establish unambiguously the analytical form of the pressure dependence of the TA(X) and TA(L) frequencies. So far it has been described with an empirical $\omega = \omega_0 + aP + bP^2$ law (where a and b are fitting parameters) with no physical justification. We have shown that this *ad hoc* description is artificial, and that the real behaviour can be

described by $\omega^2 \sim (P_0 - P)$. Germanium and probably most other tetrahedrally bonded semiconductors follow this relation to well beyond the stability region of the cubic structure, as revealed by the calculations to 25 GPa [14].

The high-pressure behaviour of zinc has attracted considerable recent interest, mostly due to a report of anomalies in the lattice dynamics detected by Mössbauer spectroscopy at 6.6 GPa [21]. This observation was attributed to the occurrence of a pressure induced electronic transition due to a change of the topology of the Fermi surface. Theory predicts a drastic phonon softening of the low energy (acoustic) phonon frequencies in such a case. High pressure neutron studies to 8.8 GPa [22] published later have claimed a « divergence » of the phonon frequencies and a possible drastic softening beyond 9 GPa.

We have investigated several acoustic modes along high-symmetry directions by inelastic neutron scattering up to 9.4 GPa on single crystals of ~ 17 mm³. The experimental set up was essentially identical with the one used for the measurements on Ge described further above. High pressure data were collected for modes along high symmetry directions Σ_1 , Σ_2 , and T_4 . Figure 5 shows constant-Q scans across the Σ_3 branch close to Γ for three pressures. This mode is identical with the one where drastic anomalies have been reported under pressure beyond ~ 6 GPa [22].

Fig. 5. Constant-Q scan at $\xi=0.075$ across the Σ_3 phonon branch for three different pressures. The line presents a least squares fit to a Gaussian including a linear background.

Despite the softness of single crystalline Zn we observed only a minor increase of the mosaic spread from 0.8° to 1° , allowing a precise determination of the frequency shifts up to the maximal pressure. The pressure dependence of this and all other measured frequencies are completely regular with no singularity occurring for any mode at any wavevector. The measured Grüneisen parameters for Σ_3 is ~ 2.9 and hence in excellent agreement with published low pressure ultrasonic measurements to 5 MPa [23]. More details will be published in a forthcoming paper [24]. These results show clearly that the proposed electronic topological transition, if it exists at all, has a minor influence on the lattice dynamics of the low-energy acoustic phonon modes.

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