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Application for beam time at ESRF – Experimental Method

This document should consist of a maximum of two A4 pages with a minimal font size of 12 pt.

Aims of the experiment

We have recently shown that Raman spectroscopic measurements can be used to study k=0 phonons in various metals at pressure in the 100-GPa regime using the diamond anvil cell (DAC) [1-8]. This proposal is to continue HS2287 Raman spectroscopic measurements of the E_{2g} phonon in hcp-structured metals with *simultaneous* x-ray studies in order to provide a secondary pressure scale based on metal-only properties. The results should offer a new pressure scale with distinct optical advantages for both P and P-T experiments. At time of writing we have beamtime at ID9 (HS2287, Feb26th-Mar2nd 2004) and have obtained the Zn (in He) x-ray structure and volume vs phonon frequency to 100+GPa. This experiment represents the *first use of an on-line raman system at ID9* and demonstrated its immediate success and potential for future work. (The raman optics are part of an in-house system made available for special research only by permission of M. Hanfland.) Samples are of order 0.020mm in size and require finest collimation of the x-ray beam: Switching between optical and x-ray modes with these small samples takes much time. We repeat the previous proposal concisely below. We do need further time to complete the programme of measurements including non-hydrostatic compression, Re metal measurements and improved spectral resolution through use of an 1800g grating. We have no beamtime report (over 3 yrs) relevant to this work, but will submit an experiment report as soon as possible after the present beam period – please check for a report at time of review.

Scientific Background

Of several available high-pressure scales, the standard ruby scale is the most widely used secondary scale in high-pressure research with the DAC. First established by Piermarini et al., in 1975 [9] and later extended by Mao et al to 100+ GPa under non-hydrostatic [10] and then hydrostatic conditions with rare gas solids as pressure-transmitting media [11], it continues to provide the basis for many experiments in the 150 GPa range and higher. A number of other materials have been proposed, e.g., $SrB_4O_7:Sm^{2+}$ [12] for high temperature-pressure experiments where there is a reduced temperature shift of the emission, as well as simple metals for x-ray and P-T studies. NaCl and a variety of other internal standards are used for x-ray experiments. Ruby remains the predominant *optical* pressure calibrant. Despite this widespread use, ruby has distinct disadvantages in ultrahigh pressure experiments: the width of the R1-R2 fluorescence region is notoriously pressure sensitive and practically limits use under non-hydrostatic conditions above 100 GPa. Errors in location of the emission maximum contribute a correspondingly large error in the pressure calculated.

Experimental method

We propose to correlate *frequency–volume* data measured by simultaneous powder X-ray diffraction and Raman techniques at the ESRF. Zn or Re are ideal candidates as pressure sensors because no phase transitions are known, or expected, to occur in the 100-GPa regime. We have found that the E_{2g} mode in these metals is intense and can be measured with our Raman techniques. A spectrometer with low-frequency capability (50-200cm^{-1}) is required. A raman-frequency-based pressure scale with a typical wave number uncertainty of 0.2 cm^{-1} based on the Zn phonon, for example, leads to uncertainties at 100, 200 and 300 GPa estimated to be 0.3, 0.4 and 0.5 GPa, respectively. This corresponds to a precision near 0.3% and rivals the most precise pressures determined by x-ray diffraction requiring a precision of 0.2% in lattice parameter determination. Our work on the Zn and Re phonons shows that they broaden much less that the R1 emission of ruby. Further, metals contribute no broad-band emission to an optical

measurement making them optically clean. The x-ray determination of volume and the raman determination of frequency can be correlated through the *a priori* shock-wave equation-of-state data available for these metals in exactly the same way as for the original ruby scale.
ID9 offers the reliable x-ray structure determination set up at high pressure (frequently used for alkali metal studies) with image-plate techniques and can supply the Raman instrument on line (M. Hanfland, personal communication). The main advantage with ESRF is the availability of high-brightness small beams and high monochromatic energies from the new in-vacuum undulator. With highly-collimated synchrotron radiation it is possible to obtain diffraction data from small sample spots of μm-size at these high pressures, which helps to further reduce the uncertainties due to pressure gradients.

To minimize pressure gradients, fluid helium (the least non-hydrostatic pressure transmitting medium besides H_2 in the 100-GPa pressure range) can be loaded into the DAC at 200 MPa in Oxford. The studies will be performed on polycrystalline foils. We can test the difference between hydrostatic and non-hydrostatic measurements directly by not using pressure media.

Results expected

Structure and coupled frequency-volume data for Re and Zn to 150 GPa.

The establishment of an international standard through the use of a metal as a pressure sensor – especially significant above 100+ GPa.

Correlation of the metal phonon measurement with the shift of the first-order diamond phonon from the anvil surface.

Frequency-volume data provide additionally a sensitive test of the accuracy of *ab initio* lattice-dynamical methods for megabar pressures [7,8].

Further extension of these measurements could establish metals as reliable pressure-temperature indicators in high-temperature DAC experiments.

Concluding Remarks

We expect to spend time aligning the laser Raman system and run both samples to the highest pressure (~150 GPa). We have estimated 18 shifts total for these experiments that might include several runs with one sample (e.g., with and without pressure media).

References

[1] H. Olijnyk, Phys. Rev. Lett. 68, 2232 (1992); Phys. Rev. B 46, 6589 (1992). **[2]** H. Olijnyk, High Press. Res. 13, 99 (1994). **[3]** H. Olijnyk, A.P. Jephcoat, Phys. Rev. B 56, 10751 (1997). **[4]** H. Olijnyk, A. P. Jephcoat, Solid State Commun. 115, 335 (2000). **[5]** H. Olijnyk, J. Phys.: Condens. Matter 11, 6589 (1999). **[6]** H. Olijnyk, A. P. Jephcoat, D. L. Novikov, N. E. Christensen, Phys. Rev. B 62, 5508 (2000). **[7]** H. Olijnyk, A. P. Jephcoat, D. L. Novikov, N. E. Christensen, Phys. Rev. B 62, 5508 (2000). **[8]** H Olijnyk, A P Jephcoat and K. Refson, Europhys. Lett. 53, 504 (2001). **[9]**Piermarini, G.J., S. Block, J.D. Barnett, and R.A. Forman, Calibration of the pressure dependence of the R_1 ruby fluorescence line to 195 kbar, J. Appl. Phys., Vol. 46, No. 6, 2774—2780 (1975). **[10]** Mao, H.-K., P.M. Bell, J.W. Shaner and D.J. Steinberg, Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R_1 fluorescence pressure gauge from 0.06 to 1 Mbar, J. Appl. Phys., Vol. 49, No. 6, 3276—3283 (1978). **[11]** Mao, H.-K, J. Xu, and P.M. Bell, Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions, JGR, Vol. 91 No. B5, 4673—4676, (1986). **[12]** Datchi, F., R. LeToullec, and P. Loubeyre, Improved calibration of the $SrB_4O_7:Sm^{2+}$ optical pressure gauge: Advantages at very high pressures and high temperatures, J. Appl. Phys., Vol. 81, No. 8, 3333—3339 (1997).

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function makeArray()
{
    for (i = 0; i<makeArray.arguments.length; i++)
        this[i] = makeArray.arguments[i];
}

var MAX = 35;

var suppliers = new makeArray(
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'ADTAH, M. ACHARD, T:04 76 48 65 56 F: 04 76 70 40 06',
'ANFI, Jacques DUJON, T:04 38 12 93 93 F: 04 38 12 93 94',
'ATEC, T:04 76 24 17 05 F: 04 76 25 31 92',
'ATELIERS PEYRONNARD, M. PEYRONNARD, T:04 76 68 88 61 F: 04 76 68 89 15',
'CHARVET, T: 04 76 46 02 45',
'CABURN MDC, C. MONTANER, T:04 37 65 17 50 F: 04 37 65 17 55',
'CALABRO, Fax: 04 76 21 49 80',
'CEPELEC, A. PAGET, Fax: 04 76 21 81 50, cepelec@club-internet.fr',
'DIFOP, J-P. PLAISANTIN, T:04 76 40 30 31 F: 04 76 40 38 65',
'DOUCET, C. BARNIER, T:04 76 84 33 70 F: 04 76 49 23 61',
'DTMI, M. JACQUET, T:04 76 50 17 00 F: 04 76 50 17 10',
'FARNELL, M. GROBON, Fax: 04 74 68 99 90, ventes@farnell.com',
'FICA, T:04 76 56 41 40 F: 04 76 75 62 33',
'FRANCE HYDRAULIQUE, M.STUDER, T:04 76 87 21 51 F:04 76 87 27 48',
<!--'GUILBERT, Mr David Blanc (david.blanc@guilbert.com), Fax: 04 72 90 23 29',-->
'GOODFELLOW, C. MUTEL, Fax: 08 00 91 73 13, mutel@goodfellow.com',
'HPC ENGRENAGES, C. JOLY, T:08 25 88 50 00 F:08 25 88 60 00',
<!--'INTERSOURCES, Mme  Dampeyroux (contact@inter-source.fr), Fax:04 76 78 60 54',-->
'ISNARD, Mme  Genevieve, Fax:04 76 85 92 13',
'JALLUT, M.VILLARD, T:04 76 24 82 24 Fax: 04 76 24 82 00',
<!--'KOETIS, Pascal LAS, Fax: 04 76 44 11 86, claudette.chardin@keotis.fr',-->
'LIGNE-APPRO, M. LENA, T:04 74 39 18 95 F: 04 74 39 24 82',
'LSGP, T:04 76 52 41 55 F: 04 76 52 41 01',
'LYON VANNES ET RACCORDS, M.FAYARD, T:04 72 37 05 70 F: 04 78 26 23 58',
'MATELECO, B. GROSSO, Fax: 04 76 70 28 98',
'MICRO MECANIQUE, Fax: 04 76 53 55 04',
'OMNI SERVICES, J.L. FARAVEL, Fax: 04 76 42 93 63, jlf@omniservices.fr',
'RADIOSPARES, M. MONTADOR, Fax: 08 25 34 50 00',
'RAYPRINT, Mme DIEN, T: 04 76 75 68 68 F:04 76 75 37 36',
'SAFIX, T:04 76 09 44 44 F: 04 76 29 41 22',
'SCHROFF, Francois PEYROT, Fax: 03 88 54 51 22',
'SMG, T:04 76 33 72 72  F:04 76 22 63 93',
'SNLS, M.GARCIA, T:04 76 38 18 33 F: 04 76 38 29 91',
'SODIPRO, A. MARTIN, Fax: 04 76 23 24 12',
'TPI, L. HUET, Fax: 04 76 84 06 62',
'VINCENT REBATET, T:04 38 24 05 05 F:04 76 49 11 36',
'WAGO, Jean-Marie Richard (info-fr@wago.com), Fax: 01 48 63 25 20');

var roids = new makeArray
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'527434',<!-- ANFI -->
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'527228');<!-- WAGO -->

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for (j = 0;j < MAX;j++)
	output += '<OPTION>' + suppliers[j] + '</OPTION>';
output += '</SELECT>';
document.open();
document.write(output);
document.close();
//-->
</script>
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