

Temperature measurement in a Paris-Edinburgh cell by neutron resonance spectroscopy

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Neutron resonance spectroscopy is demonstrated as a viable and reliable method for the determination of sample temperatures in high-pressure, high-temperature neutron diffraction studies at neutron spallation sources. The technique operates by characterizing the thermally induced Doppler broadening of neutron absorption resonances of heavy nuclei present within the sample assembly observed in transmission. Accuracies of ± 10 K have been readily achieved with data acquisition times of approximately 40 min. It is shown that the temperatures determined by this technique are independent of the sample pressure provided that the sample temperature is kept above the Debye temperature of the material whose resonances are being examined. A short list of candidate resonances for temperature measurement by neutron resonance spectroscopy is presented and suggestions volunteered for the combinations of elements most suitable for temperature measurement based on the experience of the authors. © 2005 American Institute of Physics. [DOI: 10.1063/1.2060934]

I. INTRODUCTION

The determination of sample temperatures in high-pressure, high-temperature apparatus is challenging. It is traditionally achieved through the introduction of a thermocouple, passed in between the anvils providing sample compression, through the gasketing material and embedded within the sample. This, in principle, allows the “instantaneous” determination of sample temperature through measurement of the thermocouple emf. However, the use of thermocouples for this application suffers from a number of drawbacks which may result in obtaining an erroneous measure of sample temperature or failure of the thermocouple completely.

First, as the sample assemblies used are often small, it is necessary to use thin monofilament wires. However, the addition of even very fine wires may compromise the structural integrity of the gasket, increasing the risk of gasket failure and blow outs. Additionally, the fragility of such thin wires also makes them susceptible to fracture, particularly in those regions where significant extrusion of the gasket material occurs.

Second, the thermocouple wires may constitute a significant thermal conduction path from the heated sample leading to anomalous temperature gradients within the sample. This

also brings into question whether the temperature of the thermocouple junction provides a realistic measure of the mean temperature of the sample.

Third, difficulties may be encountered with conversion of the measured thermocouple emf to temperature. For experiments conducted at ambient pressure, the measured thermocouple emf is converted to a temperature through the use of reference tables, standard conversion functions or through calibration against established reference temperatures. However, at the pressures encountered in many high-pressure studies, thermocouple emf's show significant deviations from those that would be measured at ambient pressure.^{1–4} This effect may be accommodated by applying a correction voltage appropriate to the thermocouple material used and the confining pressure.¹ Conversion to temperature may then be accomplished using the standard procedures used at ambient pressure. However, such correction data does not cover the range of pressures and temperatures under which many investigations are performed. This necessitates the extrapolation of the correction data to those conditions used, however, in doing so, an additional uncertainty in the temperature calculated must also be accepted.

Even if these difficulties are avoided, exposure of the thermocouple elements to other materials in the sample assembly at the extreme conditions produced during such experiments may lead to chemical contamination and degradation. This inevitably leads to a drift in the measured emf and ultimately, systematic errors in the temperatures obtained.

In this paper, we propose the use of neutron resonance spectroscopy (NRS) as a viable alternative to thermocouples for high-pressure, high-temperature studies using neutron

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diffraction. Neutron resonance spectroscopy as a practical technique for the noninvasive determination of sample temperature was proposed by Fowler and Taylor in work conducted at the Los Alamos National Laboratories in the 1980s⁵ and relies on the measurement of the thermally induced Doppler broadening of neutron absorption resonances. As the resonance spectrum associated with any given isotope is unique to that isotope, so specific isotopes may be identified in the measured transmission spectrum from within a multielement system. This affords the possibility of using the thermally induced Doppler broadening of absorption resonances from selected elements to provide a measure of the temperature to which they are subjected. While all isotopes exhibit resonant neutron capture, the low-energy resonances most accessible for temperature measurement are typically observed only for heavier nuclei. Unless the sample under investigation already possess such elements in its chemistry, the mechanical addition of such elements will be necessary. This mechanical addition may be accomplished by intimate mixing with the sample of a powder of a suitable element or a compound of a suitable element. Alternatively, the addition may be accomplished by including a thin foil of the element at the center of the sample assembly. Generally, as the peak cross sections for resonant neutron capture are often very large, little material is needed to provide a readily characterizable resonance line shape in the measured transmission spectrum. For example, in earlier work resonance line shapes were adequately determined for temperature measurement for a number of different elements with 50- μm -thick foils.⁶

To date NRS for temperature measurement has found few applications, in part due to: the requirement of the experiments to be conducted at neutron spallation sources; the significant acquisition times required to obtain data with counting statistics sufficient to adequately characterize the resonance line shape; and, the difficulties associated with interpreting the resonance broadening to ascertain sample temperature. Examples of studies which have used this technique include: the measurement of the surface temperature of an operating catalyst;⁷ obtaining the effective temperature of Cu atoms in a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor;^{8,9} and, characterization of the temperature behind an explosive shock front.¹⁰ NRS does, however, offer a number of potential advantages over the use of thermocouples in high-pressure, high-temperature experiments. In particular, the element added from which resonance behavior is determined is remote from the instrumentation used to characterize it. This eliminates the need for any invasive wiring passing through the gasket. This may also dramatically simplify the setup required and hence lead to significant reductions in the amount of time required to prepare each setup. Additionally, as resonant neutron absorption is a nuclear process, the resonance line shape is insensitive to changes in chemistry provided that sample temperatures are kept above those at which crystal binding effects may be observed. Indeed, there is no practical upper limit to the temperatures that can be measured with this technique and may, in principle, be performed with liquid or gaseous additions. Despite the fact that considerable data acquisition times are required to adequately characterize the resonance line shape for temperature deter-

mination, the times required are typically less than those needed to acquire suitable diffraction data. As such, the rate of data acquisition is not considered a hindrance to the application of this technique to the measurement of temperature in high-temperature, high-pressure neutron diffraction studies.

As the interpretation of the resonance line shape to obtain the sample temperature arguably constitutes the most significant challenge with the application of this technique a brief description of the theory governing resonance line shape is presented.

II. THEORY

For neutron capture by a stationary nucleus close to the energy of an isolated resonance, E_R , the reaction cross section, $\sigma_r(E)$, may be adequately described by the single-level Breit-Wigner formula.¹¹

$$\sigma_r(E) = \pi \lambda^2 g_J \frac{\Gamma_n \Gamma_r}{(E - E_R)^2 + \left(\frac{1}{2}\Gamma\right)^2}, \quad (1)$$

where E is the kinetic energy of the neutron, λ is the reduced de Broglie wavelength of the incident neutron, Γ_n is the neutron width, Γ_r is the partial width for the reaction, and g_J is a statistical spin factor for the formation of a compound state with angular momentum, J . For narrow resonances $\Gamma = \Gamma_n + \sum_r \Gamma_r$ provides a reasonable approximation.¹²

However, practical investigations seldom encounter stationary nuclei and as such it is necessary to account for the velocity distribution of the target nuclei to obtain an effective cross section, σ_{eff} . The typical approach is to define an energy-transfer function, $S(E)$.

For a monatomic free gas or classical solid, with a Maxwellian distribution of velocities at a temperature, T , the energy-transfer function becomes^{13,14}

$$S(E') = \frac{1}{\Delta \sqrt{\pi}} \exp[-(E' - E)^2 / \Delta^2], \quad (2)$$

where Δ is the so-called Doppler width and is given by

$$\Delta = \sqrt{\frac{4mME_R k_B T}{(M + m)^2}}, \quad (3)$$

where m and M are the neutron and nuclei masses, respectively, and k_B is Boltzmann's constant.

The effective cross section can then be obtained from the convolution of the Breit-Wigner formula [Eq. (1)], with the energy-transfer function,¹⁵ which leads to a well-known function.

$$\sigma_{\text{eff}}(E) = \int dE' S(E') \sigma_r(E - E'). \quad (4)$$

This line shape assumes that the absorbing nuclei exist as a monatomic free gas or classical solid. The effect of crystal binding may be accommodated by adopting a full crystal harmonic model to properly describe the resultant resonance line shape.¹⁶ However, for weak lattice binding and at temperatures in excess of the Debye temperature (T_D) of the

crystal, the resonance line shape may be adequately described by the free gas formulation with the exception that the temperature, T , in the Doppler width is replaced by an effective temperature, T_{eff} (Ref. 17) such that,

$$k_B T_{\text{eff}} = \frac{1}{2} \int d\omega \coth\left(\frac{h\omega}{2k_B T}\right) g(\omega), \quad (5)$$

where $g(\omega)$ is the phonon density of states of frequency, ω . This is the so-called effective free gas model. For pure elements above room temperature a simple Einstein model for $g(\omega)$ is sufficient and gives,^{12,18}

$$k_B T_{\text{eff}} \approx \frac{1}{2} h\omega_E \coth\left(\frac{h\omega_E}{2k_B T}\right). \quad (6)$$

Taking the first two terms of the Taylor expansion of this expression yields,

$$T_{\text{eff}} \approx T \left[1 + \frac{1}{3} \left(\frac{T_E}{T} \right)^2 \right], \quad (7)$$

where T_E is the Einstein temperature and may be related to Debye temperature ($T_E = \frac{3}{4} T_D$). From Eq. (7) it may be seen that in the high-temperature limit $T_{\text{eff}} \approx T$ as may be expected.

For measurements made at high pressures it is also necessary to ensure that the material remains in the high-temperature regime for the effective free gas model to remain valid. To demonstrate that this is the case under the conditions encountered in high-pressure, high-temperature experiments, the change in the effective temperature T_{eff} under the action an applied pressure will be estimated by accounting for the effect of the pressure on T_E .

The change in the Einstein temperature may be directly related to the change in frequency and hence also the sample pressure, P by,

$$\frac{\Delta T_E}{T_E} = \frac{\Delta \omega}{\omega} = \frac{\gamma \Delta P}{B} \quad \text{thus} \quad \Delta T_E = \frac{T_E \gamma \Delta P}{B}, \quad (8)$$

where γ is the Grüneisen parameter and B is the bulk modulus.

Taking the differential of Eq. (7) with respect to pressure,

$$\Delta T_{\text{eff}} = \frac{2}{3} \frac{\Delta T_E}{T} \frac{\partial T_E}{\partial P} \Delta P. \quad (9)$$

And, substituting for ΔT_E from Eq. (8) gives,

$$\Delta T_{\text{eff}} = \frac{2}{3} \frac{\gamma T_E^2}{TB} \Delta P. \quad (10)$$

Taking values for the Grüneisen parameter, bulk moduli¹⁹ and Einstein temperatures of transition elements, an increase in sample pressure to 5 GPa at room temperature would be expected to give rise to an increase in the effective temperature of approximately 3–11 K. Such a change is considered relatively small and may be readily accommodated in the interpretation of the resonance line shape to extract sample temperatures.

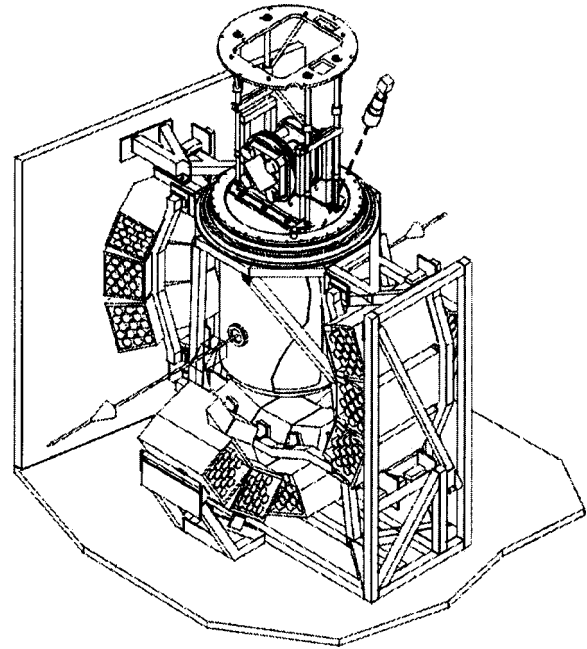


FIG. 1. Schematic of the Pearl beam line at the ISIS neutron spallation source. The Paris-Edinburgh cell and supporting frame are contained within the tank. The neutron beam passes through a channel along the axis of the cell, subsequently being diffracted to detector banks at 90° to the beam or passing through the center of the cell to a transmission detector located downstream of the cell.

III. EXPERIMENTAL DESCRIPTION

A Paris-Edinburgh cell, specially modified to allow simultaneous neutron diffraction and transmission studies at pulsed neutron sources has been developed by Le Godec *et al.*²⁰ With this apparatus pressures up to 7 GPa and temperatures of 1700 °C have been achieved with a sample volume of 65 mm³.²¹ An illustration of the cell mounted on the Pearl beam line at the ISIS neutron spallation source is shown in Fig. 1.

The cell is designed to be primarily operated with its axis aligned parallel to the direction of the incident neutron beam. In this orientation, neutrons are permitted to pass along a narrow channel through the breach of the cell to the sample assembly, passing through a small thickness of the WC anvils which provide sample compression. The neutrons may then be scattered out from the sample towards detector banks at 90° to the incident beam with cadmium on the anvil surfaces providing primary collimation. A second channel passing through the piston and back wall of the cell permits some neutrons to pass straight through the cell and sample assembly, ultimately to be collected with a dedicated transmission detector downstream of the cell. It is with this transmission detector that the neutron resonance spectra required for temperature measurement by NRS are acquired.

As discussed above, the effective free gas model offers a considerably simpler method for the determination of temperature from a measured resonance line shape than a full crystal harmonic model. It is therefore desirable to select a form for the dopant additions which fulfils the criteria of weak lattice binding and a Debye temperature below that which is to be encountered in subsequent experiments. This

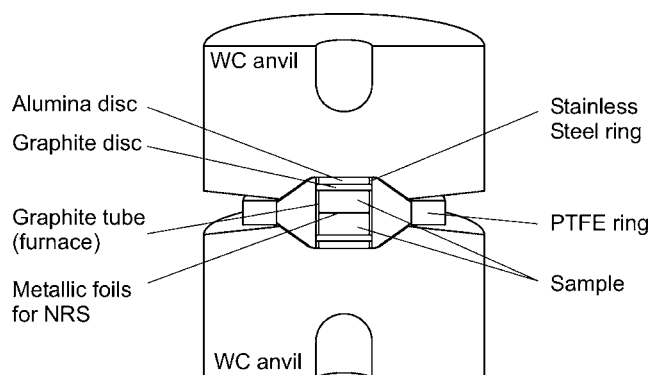


FIG. 2. Section view of sample cell assembly held between two anvils.

can be most readily achieved through the use of elemental metals. Of the possible ways by which an element may be added to allow temperature measurement by NRS (intimate mixing of a powder or inclusion of an elemental foil) it is believed that the addition of a foil is the more suitable. With a foil, control, and reproducibility of the number density per unit area of absorbing nuclei in the beam may be more readily achieved. Additionally, the criteria of weak lattice binding and a Debye temperature below that which is to be encountered in subsequent experiments is more likely to be achieved, facilitating the determination of sample temperature from the measured resonance line shape. Finally, as a foil presents a considerably smaller surface area to the sample than a powder, the extent to which chemical interaction may take place with the sample is minimized. While any such interaction would not affect temperature measurement by NRS it may have an undesired effect upon the chemistry of the sample.

Typically two or more thin metallic foils are placed in the center of the sample cell for temperature measurement by NRS. The sample cell assembly is shown schematically in Fig. 2.

Pressurization of the sample is achieved through the mechanical compression of the pyrophyllite gasket between the anvils, the efficiency of pressurization being increased through the addition of a polytetrafluoroethylene (PTFE) supporting ring.²¹ Sample heating is accomplished by thermoresistive heating of the graphite can under the application of a direct current applied across the opposed anvils. Thermal insulation of the heated sample from the anvils is provided by the inclusion of thin alumina disks.

With this cell, a number of experiments have been conducted to demonstrate the suitability of NRS for temperature measurement using the Pearl beam line at the ISIS neutron spallation source. Transmission data were gathered through a FastComTec P7888 multiscaler PCI data acquisition card in 256-ns time bins. A minimum duration of data acquisition was approximately 40 min for each sample condition. This enabled reliable characterization of the Doppler broadening of the absorption resonances. This period is smaller than that typically required to acquire diffraction spectra from samples with this apparatus which is typically from one to several hours.

IV. RESULTS AND DISCUSSION

A. Analysis of transmission data

Using the effective free gas model to provide the effective cross section, the transmission of a neutron beam for energies close to the resonance energy may be obtained from,

$$\phi(E) = \exp[-\mu\sigma_{\text{eff}}(E)], \quad (11)$$

where μ is the product of the number density of absorbing nuclei in the material per unit area and the thickness of the sample.

However, in experimentally determining the resonance line shape the effect of instrument resolution is significant and must also be taken in to account. The detected signal, $N(E)$ will therefore be

$$N(E) = P(E) \int dE' R(E') \phi(E - E'), \quad (12)$$

where $R(E)$ is the instrument resolution function and $P(E)$ is the open beam signal.

B. Determining sample temperature from the Doppler broadening of absorption resonances

Determination of sample temperature by NRS requires that the thermally induced Doppler broadening of the observed resonance may be reliably quantified from the measured resonance line shape. While a pronounced broadening can be readily observed on heating, it is typically difficult to remove the contributions of other phenomena, such as resolution broadening and variations in the amount of resonant material in the beam (e.g., from thermal expansion). A number of methods by which sample temperatures may be extracted from Doppler broadened resonances have been proposed. These include direct fitting of the observed resonance with the functions describing the line shape given in Sec. II to approaches which rely upon calibration data to extract sample temperatures. An assessment of these techniques and a critical comparison of their efficacies are presented elsewhere.⁶ In that study it was shown that the most reliable method of determining sample temperatures was by fitting the measured line shape with the analytical expressions given in Sec. II. To accomplish this, however, it is necessary to obtain reliable resonance parameters and a function that adequately describes the effect of instrument resolution on the measured line shape. With this method, separate temperatures may be obtained from each resonance in the measured transmission spectrum, which may be compared.

To examine the efficacy with which temperatures may be determined from within the sample assembly in a Paris-Edinburgh cell, a loading was examined at a series of temperatures under ambient pressure. A typical neutron transmission spectrum obtained during this experiment (with tungsten carbide anvils) is given in Fig. 3. In this example, 50- μm -thick foils of natural hafnium and tantalum have been placed at the center of the sample assembly. The stronger resonances associated with these elements from which temperatures have been determined are identified (^{177}Hf

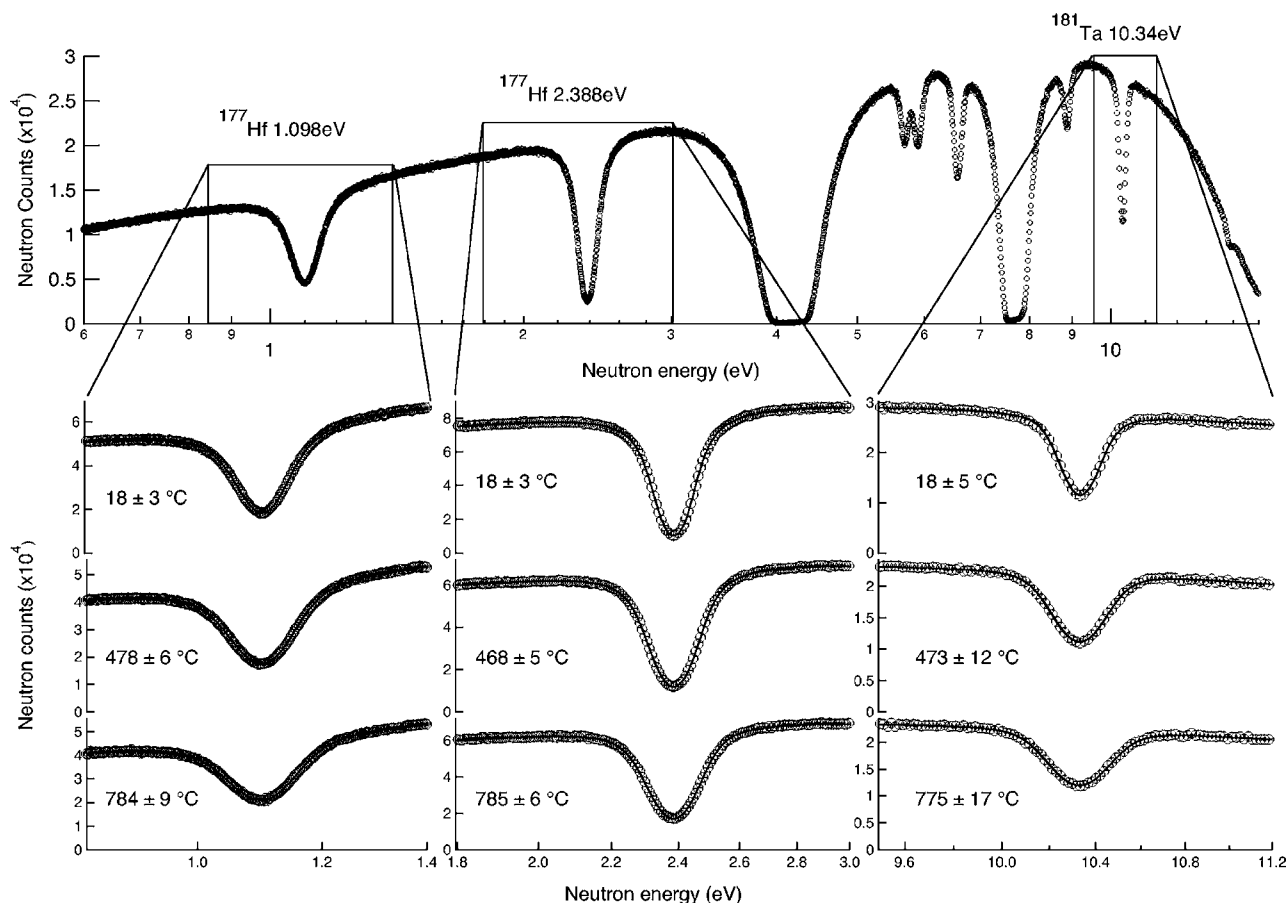


FIG. 3. Neutron transmission spectrum from the modified Paris-Edinburgh cell with tungsten carbide anvils including 50- μm -thick foils of natural hafnium and tantalum. Close-ups are included of the ^{177}Hf 1.098 eV, ^{177}Hf 2.388 eV, and ^{181}Ta 10.34 eV resonances at three temperatures including traces of the fitted line shape. For the hafnium resonance the data has been binned in to 1024-ns time bins whilst for the tantalum resonance 256-ns time bins were used. The uncertainty associated with counting statistics in the data is smaller than the symbols used and has therefore been omitted.

1.098 eV, ^{177}Hf 2.388 eV, and ^{181}Ta 10.34 eV). Note that temperatures have not been determined from the strong ^{181}Ta 4.28 eV resonance due to overlap with the ^{182}W 4.155 eV resonance from the anvils. Close-ups of the sample transmission in the vicinity of these resonances are shown for three temperatures. For the hafnium resonances the data has been binned into 1024-ns time bins while for the tantalum resonance 256-ns time bins have been used. The increase in the Doppler broadening of these resonances with increasing sample temperature is readily apparent. The measured line shapes have been fitted with the analytical expressions given in Sec. II with a Gaussian resolution function and using established neutron resonance parameters.⁶ The temperatures obtained from each resonance are given alongside each resonance with the estimated error in the temperature obtained from the uncertainty in the fitting procedure. It can be seen that the scatter between the temperatures obtained is approximately within the range that may be expected from the quoted uncertainties and is of the order of 10 K for the data acquired at elevated temperatures. This level of uncertainty is typical of that which is achieved with this technique and is considered adequate for temperature measurement in high-pressure, high-temperature experiments. It is possible to obtain higher accuracies, however, this requires increased data acquisition times to reduce the statistical errors associated with the data gathered. A more accurate measure of the

sample temperature can also be obtained by performing a weighted average of the temperatures determined from a number of different resonances.

C. Independence of Doppler width to sample pressure

While it has been shown that this technique provides an adequate measure of sample temperature at ambient pressure, to be a practical technique for the determination of sample temperature in high-pressure, high-temperature studies it is imperative that the Doppler broadened line shape of measured resonances be independent of the sample pressure. Failure to fulfil this criteria would greatly complicate the interpretation of the resonance line shape for temperature determination and bring into question the usefulness of this technique.

Characterization of the line shape at room temperature provides a stringent test of this technique as it is the lowest temperature that will be encountered in high-pressure, high-temperature experiments. As discussed in the Theory section, it is under these conditions that changes in the bonding characteristics of the resonant material, as a result of pressurization, is most likely to lead to a breakdown of the effective free gas model. For experiments conducted at higher temperatures the metallic foils used for temperature determina-

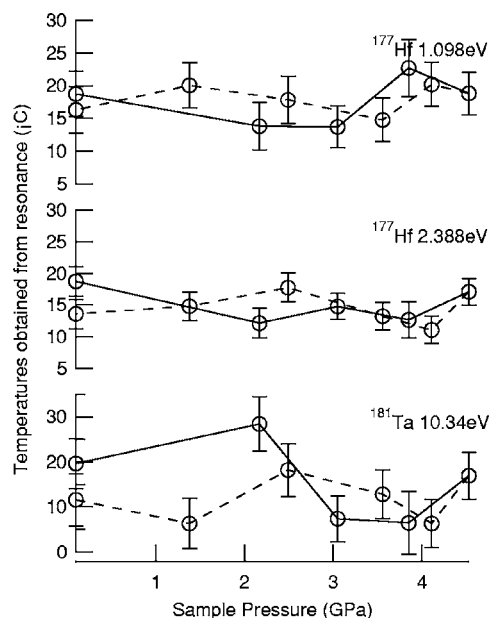


FIG. 4. Temperatures determined from the ^{177}Hf 1.098 eV, ^{177}Hf 2.388 eV, and ^{181}Ta 10.34 eV resonances as a function of applied pressure. The line between the data points indicates the path of pressurization (bold line) and depressurization (dotted line).

tion by NRS will be farther from their Debye temperatures and as such the effective free gas model will be expected to provide a better description of the resonance line shape.

To demonstrate that the Doppler broadening of absorption resonances is independent of pressure an isothermal sample loading was conducted at room temperature with 50- μm -thick foils of natural hafnium and tantalum. In this test, the sample pressure was increased to approximately 4.5 GPa before decompression. Sample pressures were determined from the diffraction pattern from a NaCl pressure marker in the sample assembly.

Any broadening or asymmetry which develops in the resonance as a result of a breakdown of the applicability of the effective free gas model with increasing sample pressure may be expected to be manifest as a systematic variation in the temperatures obtained as the sample pressure is increased. The temperatures obtained are given in Fig. 4. The line between the data points indicates the path of pressurization (bold line) and depressurization (dotted line).

The temperatures presented in Fig. 4 show no evidence of a systematic variation with pressure beyond that of experimental uncertainty. This suggests that the effective free gas model does indeed provide a reasonable method for determination of sample temperature from the resonance line shape of these elements under these conditions, as argued in the Theory section.

While no significant deviations were observed in the temperatures obtained with increasing pressure, the number density per unit area of nuclei in the beam does appear to show a pronounced variation (see Fig. 5). As with the sample temperature, this value was obtained from the fitting of the resonance line shape in which it is treated as a variable. The results from all three resonances display similar behavior with the initial number density of nuclei being greater than

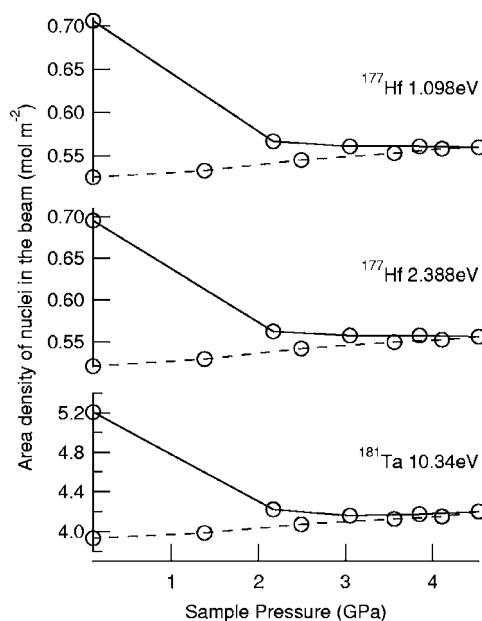


FIG. 5. Plot of the area number density of nuclei in the beam as a function of applied pressure at room temperature of the ^{177}Hf 1.098 eV, ^{177}Hf 2.388 eV, and ^{181}Ta 10.34 eV resonances obtained from 50- μm -thick foils of natural hafnium and tantalum. The uncertainty associated with counting statistics in the resonance profile is smaller than the symbols used and has therefore been omitted. The line between the data points indicates the path of pressurization (bold line) and depressurization (dotted line).

that of subsequent measurements which remain approximately constant with increasing pressure. In contrast, a slight decrease in the apparent number density is then seen during decompression. These observations may be rationalized to the extrusion and compression of material during sample pressurization. During the initial pressurization, significant movement occurs within the sample assembly as the pyrophyllite gasket deforms to transmit the applied load to the sample. This leads to the large drop seen for all resonances in the number density in Fig. 5. After this initial compaction has been produced, little movement occurs during further compression. During decompression, relaxation, and expansion of the sample may account for the small systematic decrease in the number density seen.

A consequence of these variations in the apparent amount of absorbing material is a concomitant change in the widths of the resonances (see Fig. 6). This has important implications for the method by which temperatures are extracted from the measured line shape. In the approaches of Mayers *et al.*²² and Le Godec *et al.*,²¹ temperatures are determined directly from comparison of the measured line shape to calibration data. However, in applying these approaches any change in the shape of the observed resonance arising as a result of changes in the number density of absorbing nuclei will not be accounted for and will lead to an erroneous measure of the sample temperature. For this reason, it is suggested that temperature determination by NRS in such experiments should only be performed by fitting the observed line shape with theoretical functions which can account for this effect.

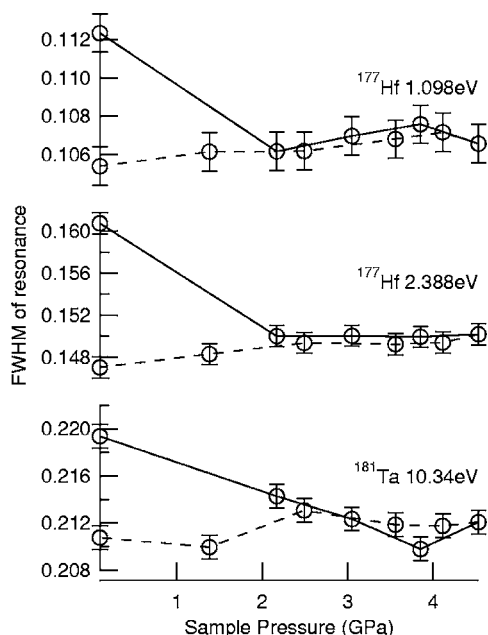


FIG. 6. Plot of the full width at half maximum as a function of applied pressure at room temperature of the ^{177}Hf 1.098 eV, ^{177}Hf 2.388 eV, and ^{181}Ta 10.34 eV resonances obtained from 50- μm -thick foils of natural hafnium and tantalum. The line between the data points indicates the path of pressurization (bold line) and depressurization (dotted line).

D. Selection of element for temperature measurement by NRS

It is apparent from Eq. (3) that high-energy resonances from heavy nuclei would exhibit the greatest Doppler broadening and hence may be expected to be the most desirable for temperature measurement. However, with such narrow, high-energy resonances greater data acquisition times are required to obtain counting statistics suitable for the accurate characterization of the resonance line shapes. Thus, in practice, temperature determination may be more readily accomplished with lower-energy resonances. We will therefore confine our interest to resonances with energies less than 12 eV. Referring to the tables of resonance parameters by Mughabghab *et al.*²³ and Mughabghab,²⁴ some 130 resonances may be identified in this energy range in 45 naturally occurring isotopes from 32 elements. However, many of these resonances may be eliminated as being unsuitable for temperature measurement by NRS or are associated with elements whose other properties make them unsuitable for inclusion in a high-temperature, high-pressure sample assembly. A number of selection criteria should therefore be applied to obtain a short list of candidate resonances. To this end, an approach similar to that used by Fowler and Taylor has been adopted.⁵

First, only strong resonances have been considered (those with cross sections at resonance >3000 b). The data acquisition times required to determine resonance line shapes of sufficient accuracy to extract sample temperatures are considerable. It is therefore important that sufficient material be added to the sample assembly such that high absorptions at resonance and hence optimum data acquisition times are achieved. It has been shown by Sears²⁵ that a transmission of 11% of the open beam is optimum for transmission measurements. Selection of foils of a thickness suitable to give this

transmission would therefore be expected to yield the greatest accuracy for temperature determination. By choosing an isotope with a large isotopic abundance and strong resonances, the amount of material that must be added to the sample assembly, to provide a resonance of sufficient depth to allow fast characterization of the line shape, may be minimized.

As will be seen, many elements offer a number of resonances suitable for temperature determination. However, as the resonances for any given element differ in strength, the foil thickness can only be optimized for a single resonance. It is therefore appropriate that the foil thickness be chosen for the resonance which will provide the most accurate and rapid determination of foil temperature. In practice this is likely to be the lowest-energy resonance of the material in question.

Second, the added element should not possess a large cross section for thermal neutron capture. If it does, the attenuation of the incident beam at the foil may alter the center of the sample as perceived by the diffracted signal detector banks at 90° to the incident beam and result in an erroneous shift in the angle at which the diffraction peaks are measured. Additionally, with significant absorption of the incident signal a commensurate reduction in the observed signal will result, increasing the time required for any diffraction measurements. For this reason, any elements with cross sections for thermal neutron capture greater than about 500 b have been eliminated.

With these selection criteria, the number of candidate resonances for temperature measurement by NRS is reduced to 28 resonances from 19 naturally occurring isotopes from 17 elements. The details of these resonances are given in Table I. The data quoted have been taken from Refs. 23, 24, and 26–29. The cross sections at resonance were calculated from the resonance parameters, accounting for the isotopic abundance.

The anvils used to provide sample compression are typically manufactured from tungsten carbide although sintered diamond anvils are occasionally used. The lowest-energy resonance in natural carbon is that of the 152.9-keV resonance in ^{13}C . This is well above the 12-eV limit imposed on the initial selection of a suitable element described above and as such any of the elements listed above may be employed for temperature measurement by NRS with such anvils. In contrast, the tungsten present in tungsten carbide anvils shows an abundance of resonances at low energies. Figure 7(a) shows the neutron resonance spectrum obtained from the modified Paris-Edinburgh cell without a sample assembly and tungsten carbide anvils. All the resonances seen in this figure arise from the tungsten present in the anvils. With such anvils, any element selected to provide temperature measurement of the sample by NRS must possess resonances away from the regions in which significant absorption of the neutron beam by the tungsten is encountered. The positions of the candidate resonances identified in Table I have been marked in Fig. 7(b). It is evident from this figure that those resonances that occur at approximately 4 and 8 eV are unsuitable for temperature measurement as they will be obscured by the overwhelming effect of the ^{186}W 4.155 eV and ^{183}W 7.63 eV resonances, respectively.

TABLE I. Data for the 28 resonances suitable for temperature determination in a Paris-Edinburgh cell from naturally occurring isotopes. These resonances are those which occur below 12 eV with absorption cross sections at resonance greater than 3000 b from elements with cross sections for thermal neutron capture less than 500 b. The data quoted has been taken from Refs. 23, 24, and 26–29.

Element	Z	A	E_0 (eV) ^a	$2_g\Gamma$ (meV) ^a	Γ_γ (meV) ^a	Abundance (%) ^b	σ_0 at E_0 (b) ^c	σ_{absorb} (b) ^d	T_D (K) ^e	T_{melt} (K) ^f
Rh	45	103	1.257±0.002	0.77±0.04	155±5	100%	5100±500	144.8	480	2237
Ag	47	109	5.19±0.01	19.1±0.6	136±6	48.16%	13000±1200	63.3	225	1235
In	49	115	1.457±0.002	3.28±0.12	72±2	95.71%	35600±2500	193.8	108	430
Cs	55	133	5.9±0.04	6.229±0.8	115±20	100 %	10800±4200	29.0	38	302
Ce	58	140	6.008±0.006	1.66±0.08	0.019±0.002	88.45%	8400±1300	0.63		1071
			6.779±0.007	0.228±0.01	0.019±0.002		41600±5900			
			8.393±0.008	1.88±0.09	0.038±0.003		10200±1400			
			11.228±0.011	0.94±0.05	0.046±0.004		16700±2400			
Ho	67	165	3.92±0.01	2.4±0.2	85±2	100 %	8900±900	64.7		1747
Er	68	167	5.98±0.02	17.7±2	84±4	22.93%	7200±1100	159		1795
Tm	69	169	3.91±0.02	12.2±0.6	96±3	100 %	33300±2700	100		1802
Lu	71	175	5.22±0.02	1.4±0.4	79±9	97.42%	4200±1600	74	210	1936
			11.2±0.02	3.1±0.4	80±7		4100±900			
Hf	72	177	1.098±0.02	1.9±0.06	66.2±0.7	18.60%	6000±300	104.1	252	2506
			2.388±0.002	9±0.2	60.8±0.7		11400±400			
			5.89±0.02	5.9±0.6	54.8±1.5		3600±400			
			7.78±0.02	100±3	60±10		22600±4800			
Ta	73	181	4.28±0.01	3.6±0.32	53±4	99.99%	18100±3300	20.6	240	3290
			10.36±0.05	3.5±0.36	65±6		6100±1400			
W	74	182	4.155±0.005	2.94±0.03	48±3	26.50%	4800±600	18.3	400	3695
Re	75	185	2.156±0.004	3.3±0.6	54.9±0.9	37.40%	12100±2300	89.7	430	3459
Ir	77	191	0.6528±0.005	0.547±0.012	72.2±0.5	37.27%	5500±200	425	420	2719
			5.36±0.01	6±0.2	82±2		5800±400			
			6.13±0.01	6.37±0.1	83±11		5200±1500			
			1.298±0.001	0.913±0.034	83.2±8		6800±1500			
Pt	78	195	11.9±0.1	15.2±1.2	112±7	33.83%	3900±600	10.3	240	2042
Au	79	197	4.906±0.01	19±0.6	124±3	100 %	30600±1800	98.65	165	1337
U	92	238	6.671±0.002	2.98±0.02	23.4±0.3	99.27%	21800±600	7.52	207	1408

^aRefs. 23 and 24.

^bRef. 26.

^cThe cross-sections at resonance were calculated from the resonance parameters accounting for the isotopic abundance.

^dRef. 27.

^eRef. 28.

^fRef. 29.

While it is advantageous to use a number of resonances from multiple elements to give a weighted average of the temperatures obtained, it is important that overlapping resonances are avoided as this complicates the determination of sample temperature. This places limitations upon the combinations of elements that are suitable for the practical application of this technique.

It may also be necessary to consider the suitability of the chemical and thermodynamic properties of the element in the environment to which it is to be subjected. For example, it may be advantageous to select a chemically inert element (e.g., Re, Ir, Pt, or Au).

For experiments conducted at low temperatures (close to room temperature) elements should be selected that possess low Debye temperatures. This will ensure that crystal-binding effects on the resonance line shape may be avoided and that the effective free gas model will provide an adequate method of determining the sample temperature. Similarly, for experiments conducted at higher temperatures it may be advantageous to choose an element whose melting temperature is well in excess of the highest temperature to be investigated. This reduces potential concern caused by the

movement of liquid material through the sample assembly which may affect the number density distribution of absorbing nuclei and hence also the observed line shape. For reference, the Debye temperatures and melting temperatures of the resonances short listed for temperature measurement by NRS are included in Table I.

Using these selection criteria, the authors offer the following suggestions for temperature measurement in a Paris-Edinburgh cell.

- For most experiments a combination of hafnium (50 μm) and tantalum (100 μm) foils is considered suitable. This permits three independent measures of sample temperature to be obtained from the ^{177}Hf 1.098 eV, ^{177}Hf 2.388 eV, and ^{181}Ta 10.34 eV resonances. Some data may also be acquired from the ^{177}Hf 5.89 eV resonance, however, this is typically too weak to determine the sample temperature accurately.
- For experiments conducted at higher temperatures (>700 K), rhenium and rhodium may be used in conjunction to provide temperature measurement from the ^{103}Rh 1.257 eV and ^{185}Re 2.156 eV resonances. If the

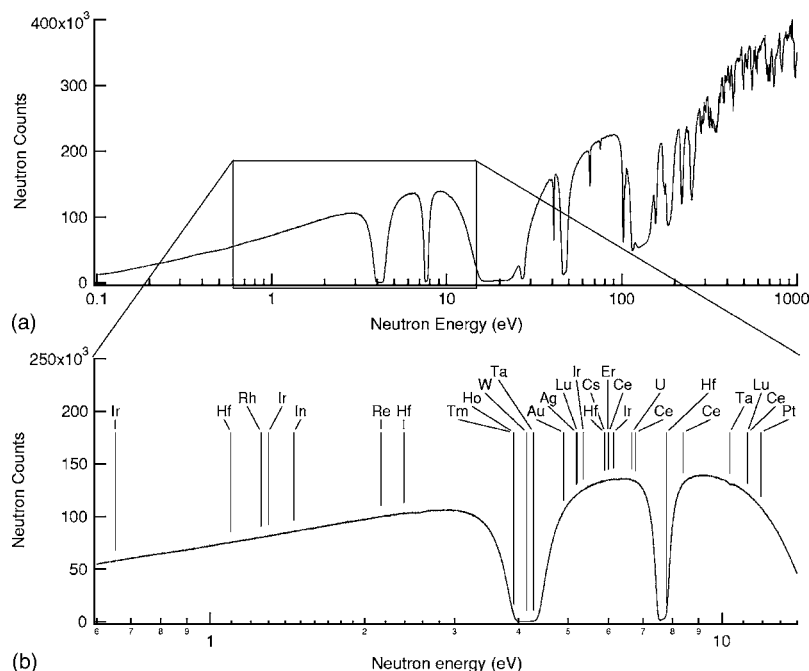


FIG. 7. (a) Neutron transmission spectrum obtained from the modified Paris-Edinburgh cell with tungsten carbide anvils and (b) Close up of neutron transmission spectrum in the 0.4–14 eV range with the positions marked of candidate resonances for temperature measurement by NRS.

maximum temperature encountered is to be less than 1200 K it is also possible to include a foil of either silver or gold thereby providing an additional resonance for temperature determination. These elements possess the additional benefit that they are chemically inert and are unlikely react with the sample.

V. CONCLUSIONS

The sample temperature in a Paris-Edinburgh cell with internal heating can be readily determined by neutron resonance spectroscopy with an accuracy of ± 10 K from a single resonance subject to good counting statistics. The accuracy with which the temperature is determined can be further improved by performing a weighted average over all the temperatures obtained from a number of resonances. The temperatures obtained are unaffected by the sample pressure provided that the sample temperature remains above the Debye temperature of the materials whose resonances are used for temperature determination.

The technique offers a number of significant advantages over the use of thermocouples. First, the element added for temperature measurement by NRS is remote from the instrumentation used to characterize it thereby eliminates the need for any invasive wiring passing through the gasket and simplifies the manufacture of the sample assembly. Second, the temperatures determined are insensitive to changes in the chemistry in the sample assembly (provided that sample temperatures are kept above those at which crystal binding effects may be observed). Finally, there is no practical upper limit to the temperatures that can be determined by this technique.

One significant weakness, however, of this technique is the time required for the accurate determination of sample temperature. For an estimated accuracy of ± 10 K to be obtained with the apparatus and source used, data acquisition times of approximately 40 min were required. This period is

smaller than that required to acquire diffraction data from this apparatus which is typically between one and several hours. Hence, while this technique for temperature measurement may be effective for such experiments the long acquisition times does eliminate the possibility of feedback control on sample heating and makes reaching a desired temperature difficult. Prompt capture gamma ray analysis, an alternative to the method described here, might alleviate some of these problems.

In spite of this limitation it is believed that the other benefits afforded by this method warrant its further use and development as a method for the determination of sample temperature in high-temperature, high-pressure experiments neutron diffraction studies.

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