

BERYLLIUM-BERYLLIUM OXIDE FILTER DIFFERENCE SPECTROMETER

by

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1. INTRODUCTION

Inelastic neutron scattering is the most important technique for the study of elementary excitations in condensed matter over a wide range of energy and momentum transfers. However, intensity limitations do, in some instances, prevent the use of inelastic neutron scattering. Since some of the new pulsed neutron sources promise to reach higher neutron fluxes than currently available at reactor based sources, the development of optimal inelastic time-of-flight (TOF) neutron spectrometers is of considerable importance. Even at the present low to medium flux pulsed sources the spectrum in the epithermal region is more intense than at high flux reactors, particularly if a hot moderator is not used. Molecular vibrational spectroscopy using inelastic incoherent neutron scattering is a natural application for this energy range whose importance has increased greatly since the Be filter inelastic spectrometer IN-1B at the hot source of the reactor of the Institut Laue Langevin (ILL) became available. The instrument described in this paper is an optimized TOF analog of the ILL spectrometer for use at pulsed neutron sources.

For inelastic scattering by TOF techniques either the incident or final flight time of the neutrons scattered by the sample must be determined separately as only the total flight time is recorded. In the Be filter spectrometer the final energy of the neutrons reaching the detector is less than the polycrystalline cutoff (5.22 meV) which gives a wide bandpass of final flight times. The resulting count rates are therefore much higher than those of a crystal analyzer whose bandpass is defined by the crystal mosaic and the range of Bragg angles available to the scattered neutrons. Furthermore, since the final energy for a filter analyzer is small compared to the incident neutron energy for measurements of large energy transfers,

the momentum transfer Q does not vary much with scattering angle. A large solid angle can therefore be covered with adequate Q -resolution. This type of spectrometer is however most useful for the study of essentially dispersionless excitations, since it effectively allows only one cut through (Q,E) space.

A large improvement for the filter spectrometer is possible by taking the difference of spectra recorded with two different filter materials. The instrument described in this paper utilizes as the bandpass of final energies the difference between the cutoffs of Be and BeO of 1.5 meV. A schematic of the spectrometer is shown in Fig. 1. The filter sections are arranged in an alternating sequence of beryllium and beryllium oxide, five on each side covering a range of 90° in scattering angle on each side. The physical dimensions of a section are: inner radius 90mm, outer radius 240mm, angular spread 18° and height 100mm. The sample position is 13m from the target and the detectors are 0.28m from the sample. Each detector bank consists of six ^3He 10 atm detectors. The beam size is 25mm x 100mm at the sample position. Each bank is separately recorded, like filter material spectra summed, and the weighed difference taken.

We begin by giving a description of the data analysis for a simple filter analyzer, followed by a discussion of the difference method. The filter difference technique is then compared with the single material filter and the current Weapons Neutron Research (WNR) crystal analyzer. A brief survey of experiments conducted with the difference spectrometer is presented in section 4. Finally, the expected types of use of this instrument in future high intensity operation are discussed.

2. SINGLE FILTER MATERIAL

Before proceeding with taking the difference of two filter materials it is important to understand the lineshape and resolution of spectra taken with a single filter material. In a TOF experiment the bandpass of the polycrystalline filter material is measured on a time scale, not an energy scale as in a reactor experiment. The observed inelastic spectrum is a convolution of the instrumental resolution, the response function of the excitation being measured and the filter response function. First, the instrumental time resolution may be described by an effectively gaussian lineshape. Contributions to it include the moderator pulse width, the proton burst width, the sample size, and the width of the filter edge. The intrinsic lineshape from many types of excitations can be assumed to be a lorentzian in energy, for which a lorentzian in time is a reasonable approximation. Finally the filter transmission is not an ideal step function especially for a filter length sufficient to prevent leakage of neutrons above the filter edge. A finite cross section remaining for energies less than the filter edge attenuates the beam. The transmission function has the form

$$T \propto \left(\frac{t_e}{t} \right)^4 \exp(-\beta dt/L) \quad (1)$$

where t_e is the time-of-flight from the sample to the detector for neutrons of the edge energy, β the absorption coefficient, d the filter length, L the distance from the sample to the detectors, and t the time-of-flight from the sample to the detector for a neutron of an energy less than the filter edge.

The lineshape resulting from the convolution of the three contributions is quite asymmetric with a steep rise on the short time side and a tail on the long time side (see figure 2a). The fit to the data shown in Fig. 2a

shows that this model for the filter lineshape yields reasonable parameters at least for isolated peaks. Not shown is the fit to the BeO spectrum, which is in excellent agreement with the fit to the Be spectrum. Thus we can consider spectra taken with a single material filter to be well understood.

These spectra, however, have some disadvantages which limit the usefulness of such a spectrometer. The relatively poor resolution makes deconvolution of overlapping peaks difficult, particularly if a broadened peak shows no obvious structure. A practical upper limit of three lorentzians in a convolution reduces the information obtainable from a complex spectrum such as that shown in figure 3a. The most disturbing aspect of the model is that the shift of the peak position resulting from the convolution is dependent on the intrinsic width of the mode being measured. The time-to-energy transformation is therefore very complex.

3. DIFFERENCE METHOD

Some of the complications and restrictions of the single filter spectra may be overcome by combining data using filters with two different cutoff energies such as Be and BeO. The bandpass is then restricted to the energies between the two cutoffs (3.76 to 5.22 meV). While this is important, the main improvement results from the elimination of the long low energy tail present with the single filter material.

The most important problem for the difference method is to subtract the two spectra correctly. For physical considerations the filters were selected to be the same length and the detectors all the same distance from the sample. In order to perform the difference, the transmission fractions for the two filters should be matched for energies below that of the BeO edge. Using Eq. 1 of section 2, we require that

$$\alpha T(\text{Be}) = \alpha' T(\text{BeO})$$

or

$$\alpha \left(\frac{t_e}{t} \right)^4 \exp(-\beta dt/L) = \alpha' \left(\frac{t'_e}{t'} \right)^4 \exp(-\beta' d't/L')$$

where the primed values refer to the BeO. Since d and L are the same for both materials, then

$$\frac{\alpha'}{\alpha} = \left(\frac{t_e}{t'_e} \right)^4 \exp[-d(\beta - \beta')t/L]$$

giving $\alpha'/\alpha = 0.58$ at the Be edge. Although α'/α is still a function of t , its dependence over a peak is weak and may be replaced by a weighted mean $\overline{\alpha'/\alpha} = 0.60$. This is in excellent agreement with transmission measurements made on two sections at WNR which yielded a mean ratio of 0.60.

While taking the difference leads to a loss in statistical accuracy, the high throughput of the spectrometer nevertheless allows a few percent statistics to be collected in a reasonable amount of time. The advantages gained however are considerable. First, a symmetric lineshape (see Fig. 2b) is recovered because the bandpass between the two filter edges is nearly a square function. Second, the greatly improved resolution allows peaks which are not obvious in the undifferenced spectra to be discerned. An example is given in figures 3a and b where the Be filter spectrum and the difference spectrum of potassium hydrogen maleate are shown. Finally, the time to energy mapping is no longer dependent on the intrinsic width of the vibrational excitation. Fitting can now be performed outside the convolution, which is needed in the undifferenced case, and can be done on an energy rather than a time-of-flight scale.

The resolution of the filter difference spectrometer is compared (Fig 4.) with that of the crystal analyzer spectrometer currently in use at the WNR. At energy transfers greater than about 100 meV the resolution is similar to that of the crystal analyzer, but the count rate significantly is higher because of the larger solid angle covered and the wider bandpass of final energies.

4. EXPERIMENTAL PROGRAM

The present experimental program using the filter difference spectrometer at the WNR consists of the following areas.

(1) A principal application has been the study of localized hydrogen vibrations in metals, particularly the bcc hydrides such as Nb and Ta. In this case the aim is to relate vibrational energy levels to anharmonicity of the hydrogen potential. A program in cooperation with Sandia National Laboratories has been initiated on rare earth metal hydrides. The vibrational frequencies and relative occupation of tetrahedral and octahedral site hydrogen atoms have been measured for concentrations near the dihydride for lanthanum and yttrium (see Fig. 5). In addition, the hydrogen storage material FeTi was studied.

(2) The vibrational frequencies of H in extremely short intramolecular hydrogen bonds were determined for a number of such compounds in a collaboration with the University of Durham, U.K. (see, e.g. the spectrum of KH maleate, Fig. 3b). The resulting correlation of the out-of-plane bending mode $\gamma(\text{OH})$ with the O-O distance is completely different than that found in many previous studies for the usually longer intermolecular hydrogen bonds.

(3) A series of experiments were conducted to study the coupling of torsional modes of NH_2 and NH_4 groups to other internal modes in

insensitive high explosives such as picrates, triaminotrinitrobenzene and related compounds (Fig. 6). Torsional modes could readily be identified, and pronounced frequency shifts were observed as a result of the intramolecular mode coupling.

(4) Catalytic reactions can be studied on large surface area materials owing to the penetrating power of neutrons in comparison to electrons or light. Preliminary experiments on organometallic compounds such as $\text{Mn}(\text{CO})_5\text{CH}_3$ and $\text{HCCo}_3(\text{CO})_9$ to observe C-H modes have been performed. Work is also in progress on ethylene on a supported platinum catalyst in collaboration with Brookhaven National Laboratory.

5. CONCLUSIONS

A successful experimental program has been initiated on the filter difference spectrometer. The instrument is most appropriate for energy transfers from about 50 to 600 meV when moderate energy resolution is sufficient and a high count rate of importance. The difference technique is well enough understood so that peak positions, line widths and integrated intensities can be determined from fairly complex spectra.

Several improvements to the instrument are in progress. An important change will be cooling of the sections which is expected to give approximately a factor of two increase in signal. The solid angle subtended by the detector banks will also be increased by a factor of 1.7 without significant degradation in resolution. With these improvements, much smaller samples can be examined in cases where material is unavailable in larger quantities, as well as samples with much small scattering cross sections.

The major improvement will come when the proton storage ring becomes operational in 1985. A total increase of approximately 100 in neutrons detected will allow much more difficult experiments to be performed on this instrument with still a fast turnover rate.

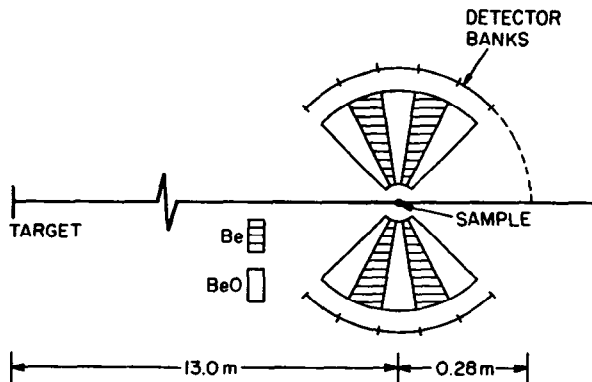


Fig. 1

A schematic of the filter difference spectrometer is shown. Filter sections are 150mm long, 100mm high and span 18 degrees. Each detector bank consists of six ^3He 10atm detectors.

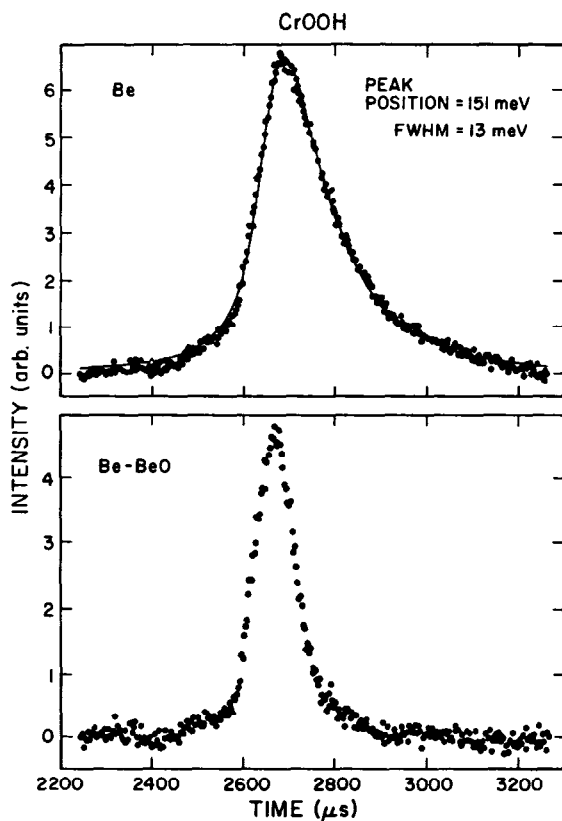


Fig. 2. (a) Chromous acid spectrum from the beryllium filter data and the fit given by the solid line. (b) Chromous acid difference spectrum. Notice the missing tail on the long time side of the peak.

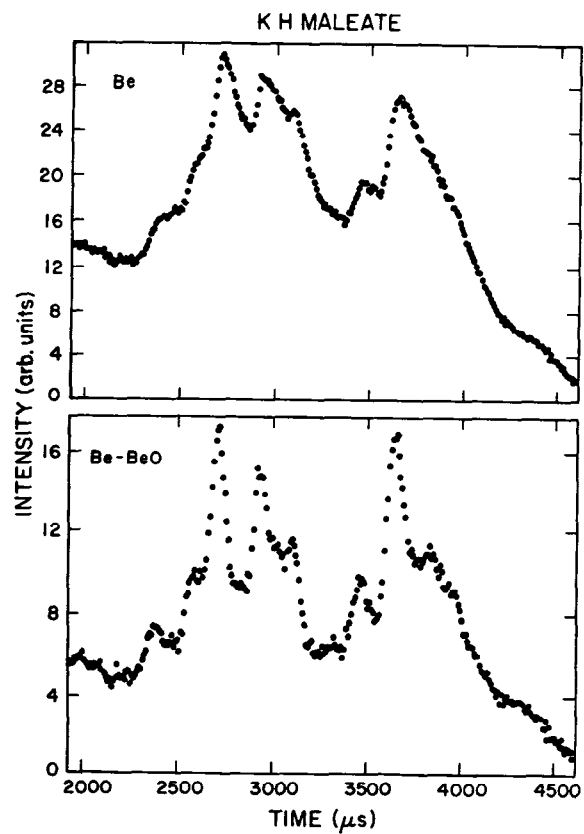


Fig. 3. (a) Beryllium filter spectrum of potassium hydrogen maleate. (b) Difference spectrum of potassium hydrogen maleate. The peak at 2,500 μs is $\gamma(\text{OHO})$ mode.

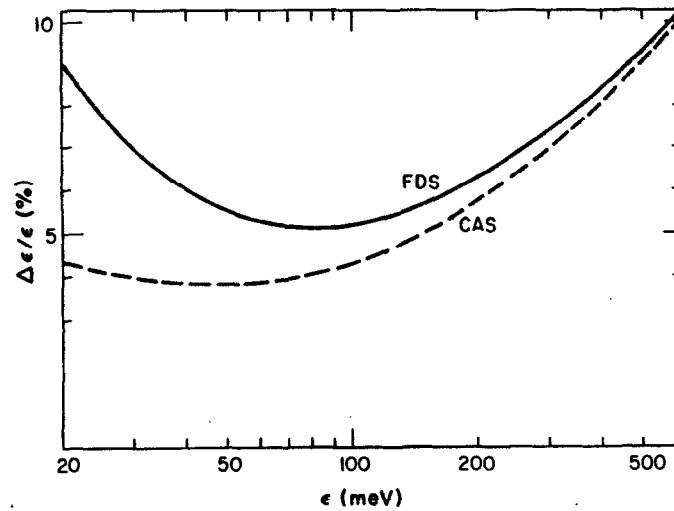


Fig. 4. Energy resolution (FWHM) of the filter difference spectrometer (FDS) and the WNR crystal analyzer spectrometer (CAS).

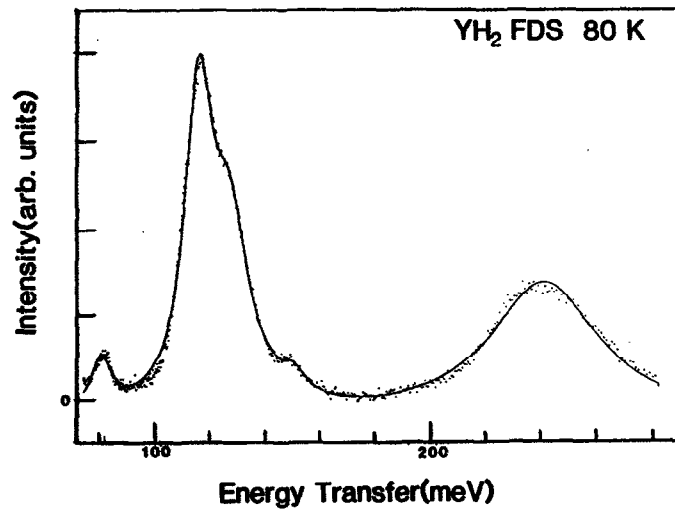


Fig. 5. Yttrium dihydride spectrum taken on the filter difference spectrometer. The peak near 80 meV is due to octahedral site hydrogen atoms while the one at 120 meV is due to tetrahedral site atoms.

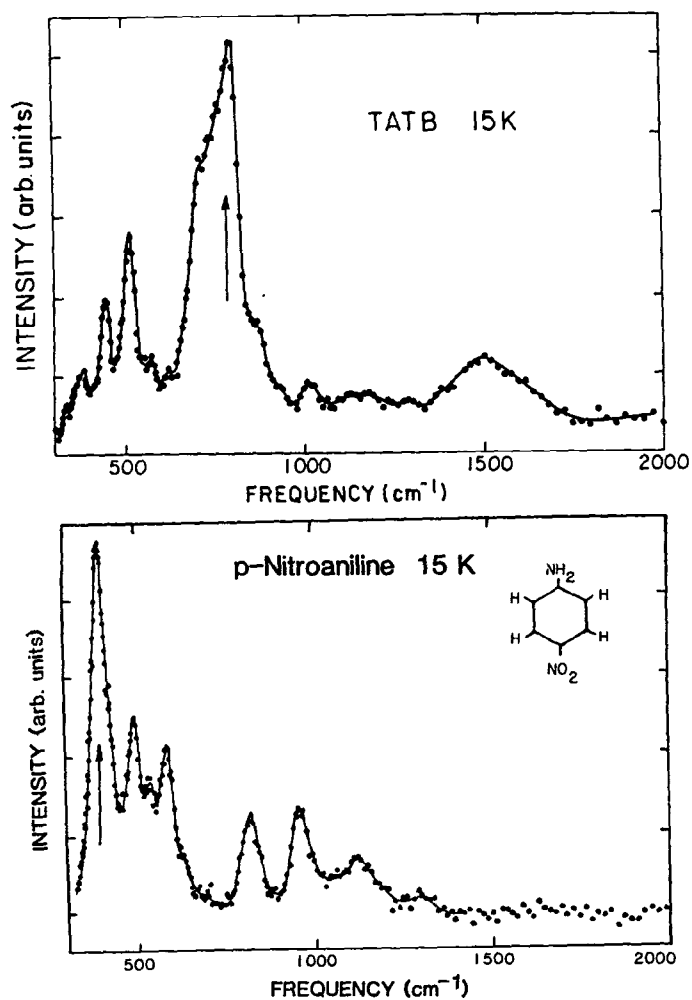


Fig. 6

1, 3, 5-triamino 2, 4, 6-trinitrobenzene (TATB) and para-nitro-aniline are shown. The NH_2 torsional frequency (arrows) is significantly higher in TATB where strong coupling to the NO_2 groups is suspected.

Fig. 7

Tricobalt-nonacarbonyl-methylidyne difference spectrum showing the H-C bending mode at 105 meV, a C-Co stretch at 86 meV and their harmonics at 172 and 210 meV. The modes between 50 and 70 meV are Co-C-O and Co-Co modes.

