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TITLE: CONDENSED-MATTER RESEARCH AT THE LOS ALAMOS PULSED NEUTRON SOURCE (WNR)

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ABSTRACT

The experimental program at the WNR in condensed matter research at present is aimed principally at utilizing the high epithermal neutron flux available at a spallation neutron source. Interesting new results have been obtained in several areas including hydrogen vibrations in metals, chemical vibrational spectroscopy and the structure of liquids. For example, extensive vibrational spectra were obtained of hydrogen in Nb which could be described in terms of a three-dimensional localized anharmonic oscillator, deuterium substitution methods were used to determine the variation with O-O distance of the hydrogen bending mode frequency in extremely short intramolecular hydrogen bonds, nd model-independent partial structure factors were determined for liquid water.

I. INTRODUCTION

It has long been expected that the advent of high intensity pulsed spallation neutron sources will open up new areas of neutron scattering research in condensed matter[1]. There are at least two reasons for this expectation: first, the neutron spectrum of such a source falls off as 1/E for epithermal neutrons as compared with the exponential decrease of the Maxwellian reactor spectrum. Thus enormous increases in the flux of epithermal neutrons can be realized at a spallation source, with which the useful energy-momentum space is similarly increased. Secondly, it has been argued [2] that spallation sources may be the way to achieve much higher fluxes of thermal neutrons than is practicable with reactors. Experiments that at present are count rate limited (e.g. small samples, low scattering cross section) may then be attempted at the pulsed spallation sources provided that time-of-flight techniques can be optimized to make use of the high peak neutron fluxes.

Since the Los Alamos spallation neutron source (WNR) will not reach its nominal peak thermal flux of 10^{16} neutrons/cm^2.sec until the operation of the proton storage ring (PSR) begins in 1985 the scientific interest in its use at this time lies primarily in the high epithermal neutron flux. The experimental program at the WNR has therefore concentrated on utilizing the high energy neutrons while developmental programs are also aimed at producing novel time-of-flight instrumentation to operate in the thermal neutrons energy range as well. An example of the latter is the so-called "constant-Q" spectrometer [1,3] which will permit the measurement of dispersion relations (phonons, magnons) in much the same way as a triple-axis spectrometer at a reactor source with complementary resolution characteristics.

The availability of large numbers of epithermal neutrons would also allow higher energy transfers to be reached.

In the former category are two neutron energy loss inelastic spectrometers, the crystal analyzer (CAS) and filter difference (FDS) spectrometers, as well as the general purpose diffractometer (GPD). The latter can reach large momentum transfers at small scattering angles because of the epithermal neutrons. Inelasticity corrections to the structure factor measurements can thereby be minimized.

A review is given in this paper of some of the results obtained on these three instruments. The inelastic scattering studies concern mostly dispersionless high energy vibrational excitations in metal hydrides [4] and hydrogen bonded materials [5] The diffraction study [6] to be discussed is a new determination of the hydrogen-hydrogen pair correlation function in liquid water. Work is also in progress at the WNR on single crystal diffraction and neutron eV spectroscopy using nuclear resonances, but will not be covered in this review.

II. ANHARMONICITY OF THE H POTENTIAL IN Nb

Information on the H-metal interaction between interstitial H and its metal atom neighbors is of considerable importance for the understanding of H diffusion in metals and ultimately the H storage properties of metals. Inelastic neutron scattering is the only direct spectroscopic technique for observing H vibrations in these systems, and extensive efforts have been made to learn details of the H potentials by this method [7]. Of particular interest have been the bcc metal hydrides, such as NbH_x, since they exhibit quantum mechanical diffusion [8] in

addition to ng suitable model systems. In such a case the measured activation energy for diffusion is not directly related to the potential barrier height. One may then obtain an approximate idea of the depth as well as the shape of the H potential using inelastic neutron scattering to measure the harmonic oscillator transitions of the H interstitial. However, previous such efforts have only been partially successful, as the large energy transfers necessary are difficult to reach with good energy resolution at reactor neutron sources.

In particular, in the case of NbH_x (or the similar system TaH_x) where the H vibration is split into a singlet at about 120 meV and doublet (at about 165 meV) because of the tetragonal symmetry of the tetrahedral interstitial site, only the 0-1 transitions for the singlet and doublet and the 0-2 transition for the singlet could be determined in previous studies [7]. Substitution of deuterium for hydrogen can give further information about the potential well, as the frequencies shift as $1/\sqrt{M}$ if the potential is harmonic. The utility of this approach depends on the assumption that the H-Me and D-Me interactions are the same, which appears to hold fairly well [4] for NbH(D) and TaH(D). The results of the neutron scattering studies of H in Nb and Ta have therefore only been interpreted in terms of a single anharmonicity parameter [7] for the singlet vibration treated as a one-dimensional anharmonic oscillator. In addition, as far as the depth of the potential well is concerned, one may only say that it is larger than the highest transition observed (viz. about 230 meV) which already is some 50% greater than measured activation energies for diffusion [8].

More extensive measurements on these bcc hydrides would therefore be quite desirable. Of particular interest is also the question of whether anharmonicity couples the singlet and doublet vibrations. If such a coupling is of comparable magnitude as the anharmonicity determined in the singlet vibration above, the latter treatment is no longer adequate. We have therefore undertaken extensive studies at the WNR of NbH_x and TaH_x with the aim of developing a more complete picture of the anharmonicity in the H potential. In addition a large amount of effort was made to relate observed broadening and/or structure in the vibrational transition lines to phase changes occuring in the high concentration, low temperature portion of the NbH_x phase diagram [9]. This is possible by noting that changes in the symmetry of the H site and the H-Me distances will shift the vibrational frequencies of the H. In addition, since coherent inelastic neutron studies on NbD_x single crystals have not shown any significant dispersion in the optic phonon branches, changes in the transition lineshapes at low temperatures can often be explained in terms of structural changes. For further details of this part of the NbH_x studies the reader must be referred to a forthcoming article [4].

Shown in Fig. 1 is the inelastic incoherent neutron scattering spectrum of $NbH_{0.95}$ at 15K obtained on the CAS at the WNR. Apart from the strong singlet and doublet lines of the transitions to the first excited state at 122 and 166 meV respectively, additional structure is discernible at larger energy transfers. It consists of a well defined line at 231 meV corresponding to the 0-2 transition of the singlet vibration, a combination band at 280 meV, presumably followed by the

unresolved 0-3 singlet and 0-2 doublet transitions. Along with similar data on samples with different concentrations these results could be interpreted in terms of a three-dimensional anharmonic oscillator with tetragonal symmetry ($\bar{4}2m$), the tetrahedral site in the bcc structure. In this case there are a total of five anharmonic terms of third and fourth powers in the displacements:

$$H_1 = ez(x^2 - y^2) + c_{4,z}z^4 + c_{4,x}(x^4 + y^4) + fx^2y^2 + gz^2(x^2 + y^2)$$

where the z-direction corresponds to the singlet vibration. The second term is the only one that has been included in the previous analyses [7]. H_1 can be treated as a perturbation on the harmonic Hamiltonian. The resulting expressions for the peak positions of the transition lines are given in Ref. 4. While data such as that shown in Fig. 1 is still not extensive enough nor of sufficient accuracy to determine all the coefficients in the anharmonic Hamiltonian above, a second anharmonicity parameter f in addition to $c_{4,z}$, could be determined by these experiments. f is a measure of the strength of the coupling between the singlet (z) and doublet (x,y) vibrations. It was found to be of comparable magnitude than the anharmonicity in the z-vibration. The earlier approaches of treating the z-vibration separately are therefore not applicable in this case, and are only reasonable if the value of f is much less than the anharmonicity of the singlet vibration. This model was also used to give a consistent account of previous data, including the isotope shifts [10] in β-NbH_x (D_x,T_x).

As far as the height of the potential barrier for the H is concerned the present data allow only the conclusion that it must be greater than

about 350 meV. Further transitions may simply have too low an intensity to be observed. However, even the value of 350 meV is considerably larger than a recent theoretical estimate [11].

III. INTRAMOLECULAR HYDROGEN BONDS

While the utility of incoherent inelastic neutron scattering in focusing on those molecular vibrations that involve a large amplitude H-motion is well known, applications of this technique have concentrated on low energy excitations, such as rotational tunneling transitions [12]. The availability of the inelastic neutron spectrometer at the hot source of the Institut Laue Langevin has, however, given significant impetus to molecular vibrational spectroscopy with neutrons. Pulsed neutron sources with their larger numbers of epithermal neutrons may therefore be expected to have an even greater impact in this area.

Neutron molecular vibrational spectroscopy is particularly effective as a complementary tool to light scattering in cases where modes are IR and/or Raman inactive or where assignments are difficult because of the presence of strong interactions between modes. A further application of neutron scattering is the area of vibrational spectroscopy of molecules on surfaces where the simultaneous presence of large amounts of substrate materials makes light scattering difficult. Particularly attractive is the possibility of studying the progress of catalytic reactions by identifying characteristic vibrational lines of intermediate species.

Efforts are underway at the WNR in all these areas of molecular vibrational spectroscopy. An extensive comparative study on $CH_3Mn(CO)_5$ involving IR, Raman and neutron scattering [13] has been completed as a

preliminary step towards the study of absorbed molecules. Current experimnts involve a supported Pt catalyst. Mode assignments in the compound TATB(1,3,5-Triamino - 2,4,6 Trinitrobenzene) have been extremely difficult in the light scattering experiments because of extensive mode mixing. A series of neutron scattering studies on this and the related compounds 2,6-Dinitroaniline, p-Nitroaniline and p-Chloroaniline [14] has demonstrated this coupling and helped in the mode assignments for TATB.

The understanding of hydrogen bonding has been significantly advanced by systematically relating the vibrational frequencies of the H in the bond to structural data. Particularly, a large amount of data on intermolecular hydrogen bonds has been summarized [15] in a correlation of the out-of-plane bending mode, γ(OHO), vs. O-O distance, R(OO). The approximately linear increase of γ(OHO) with decreasing R(OO) found seems reasonable in that the H potential may be expected to deepen as the two O atoms approach one another. There has been much speculation along with this empirical correlation on the possible existence of a physical low limit for an unconstrained hydrogen bond [15]. In fact, intermolecular hydrogen bonds with R(OO) < 2.4 Å are not known.

There are, however, molecules with very short intramolecular hydrogen bonds [15,16]. In these case R(OO) is typically constrained by a ring structure of the molecule. Partly because of the symmetry properties of these molecules light scattering techniques have not been useful in the mode assingments. Inelastic neutron scattering has however been successful in identifying γ(OHO) as well as the other normal modes of the hydrogen bond. An example of the isotopic substitution technique is shown in Fig. 2 where with the replacement of the H in the bond with D

results in the absence of the second line of the doublet near 130 meV for Ni-Dimethylgloxime.

The results [5] of a systematic study at the WNR of a number of compounds with intramolecular hydrogen bonds of R(OO) < 2.44Å showed that in contrast to the case of the longer intermolecular hydrogen bonds γ(OHO) decreases with a further decrease of R(OO). It therefore appears that a fundamental change in the dynamic properties of the hydrogen bonds occurs at about 2.4Å, as several other possible explanations of the different correlations (such as the planarity of the bond) can be ruled out [5].

IV. HYDROGEN-HYDROGEN CORRELATION FUNCTION IN WATER

The determination of H-H pair correlation functions in liquids using diffraction techniques is complicated by the problem that H will recoil significantly when scattering a neutron, particularly at large momentum transfers. Since it is necessary to perform a Fourier transform of the partial structure factor in order to obtain the radial distribution function $g_{HH}(r)$ the measurements have to be extended to large values of Q. The recoil, or inelasticity, has to be corrected when analyzing such data, and usually requires the introduction of a model of the inelastic scattering. It may, however, be shown that inelasticity can be minimized by scattering at small angles neutrons with large incident wave rector to reach large values of Q. Pulsed neutron sources with their high flux of epithermal neutrons are therefore ideally suited for this type of experiment.

In order to extract the H-H pair correlation function an isotopic substitution technique is used. In this case the differental cross

sections were measured for H_2O , D_2O and an H_2O : D_2O mixture. Because of the rapid H,D exchange the last of these is equivalent tc using HDO. The distinct partial H-H scattering cross section can then be obtained from

$$x\Sigma^{H_2O}(Q) + (1 - x)\Sigma^{D_2O}(Q) - \Sigma^{H_2O : D_2O}(Q) = 4x(1 - x)(a_H - a_D)^2\Sigma^{d}_{HH}(Q) + \Delta$$

where x is the proportion of H_2O in the mixture, a_H and a_D the respective coherent scattering lengths and Δ correction terms, which were calculated to be negligible in this case [6]. The three data sets were collected on the GPD at WNR using a low scattering angle of 40^o to assure that inelasticity corrections would be small.

Once the partial H-H structure factor has been obtained as described above it can be Fourier transformed to give the radial distribution function $g_{HH}(r)$ shown in Fig. 3. The experimental results can then be compared with theoretical works, two of which are also shown in Fig. 3: the molecular dynamics simulations by Lie, Clementi and Yoshimine (LCY) [17] and by Rahman and Stillinger [18] using the ST2 potential. The agreement with the experiment by Soper and Silver [6] can be seen to be remarkably good. The first two peaks of the intermolecular part of $g_{HH}(r)$ are shifted to slightly smaller values of r in the experiment and the minimum between the two is deeper. This implies that the nearest neighbor shell is more tightly coordinated than the theoretical results

suggest, which can also be illustrated by computing the coordination number of the first peak. The data of Soper and Silver [6] yield a value of 5.7 which may be compared with 6.1 and 6.5 for the LCY and ST2 calculations respectively.

V. CONCLUDING REMARKS

This review has shown that even while the WNR is still in a developmental stage the pulsed source spectrum can already be used for interesting new research in condensed matter. With the projected large increase in neutron flux the WNR/PSR and similar high intensity spallation sources may therefore be expected to substantially increase the importance of neutron scattering techniques.

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RUNNING TITLE: CONDENSED MATTER RESEARCH AT WNR

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Hydrogen Bond
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FIGURE CAPTIONS

1. Inelastic neutron scattering spectrum of $NbH_{0.95}$ at 15K measured on the CAS. Data has been reduced to represent $S(Q,\omega)$.

2. Determination of the out-of-plane bending mode frequency of the hydrogen bond in Ni-Dimethylgloxime by deuterium substitution using the FDS at WNR.

3. H-H radial pair distribution function obtained from neutron diffraction studies on water using the GPD (solid circles). The dashed and solid lines represent theoretical calculations (see text).

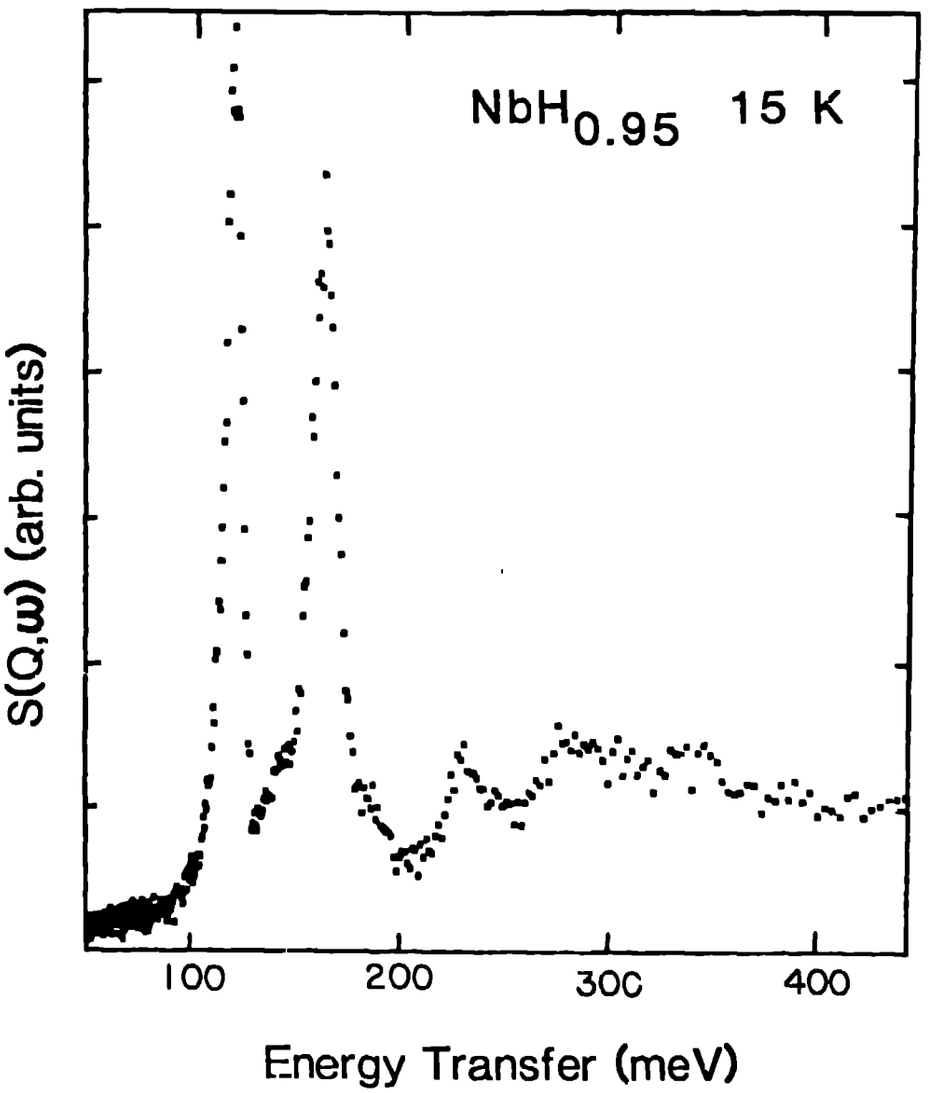
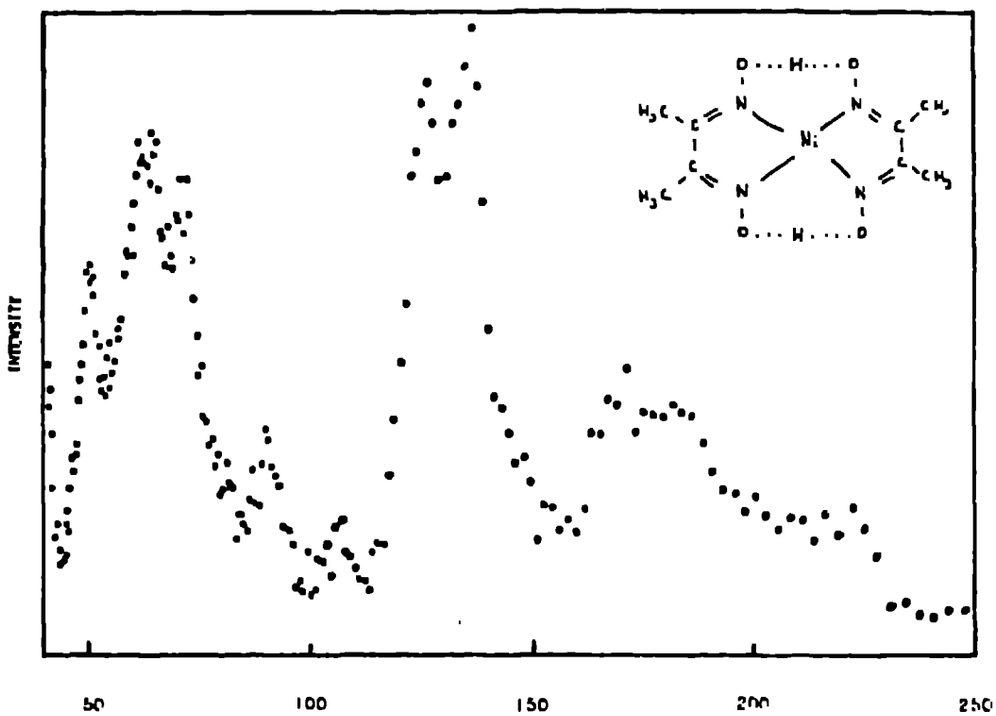
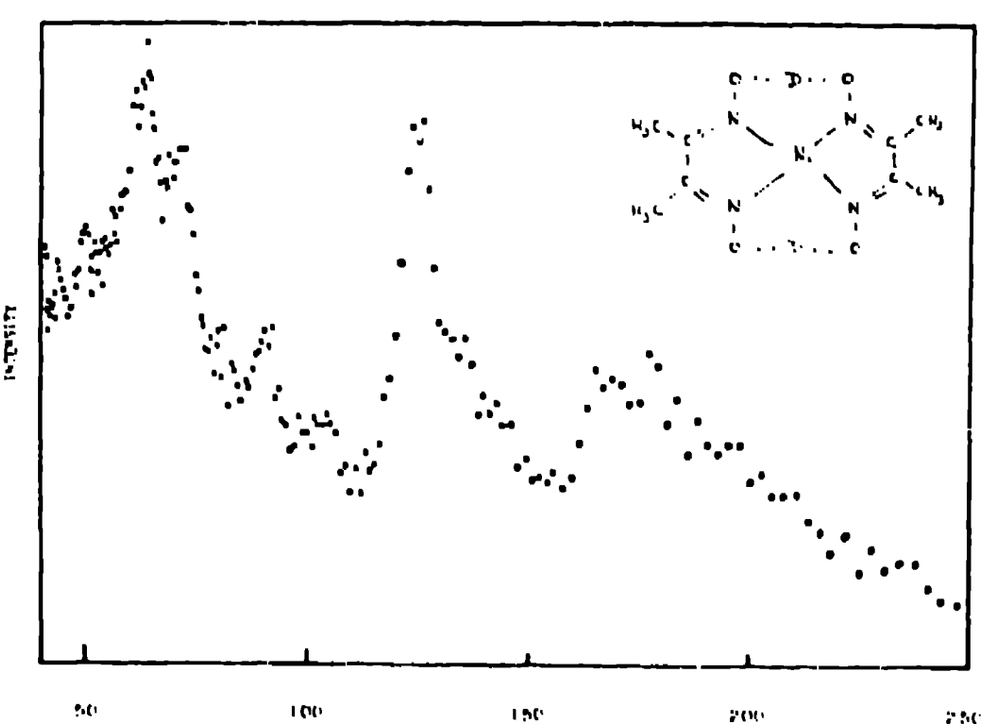


FIGURE 1

Ni-DMG2:H



Ni-DMG2:D



ENERGY TRANSFER meV

FIGURE 2

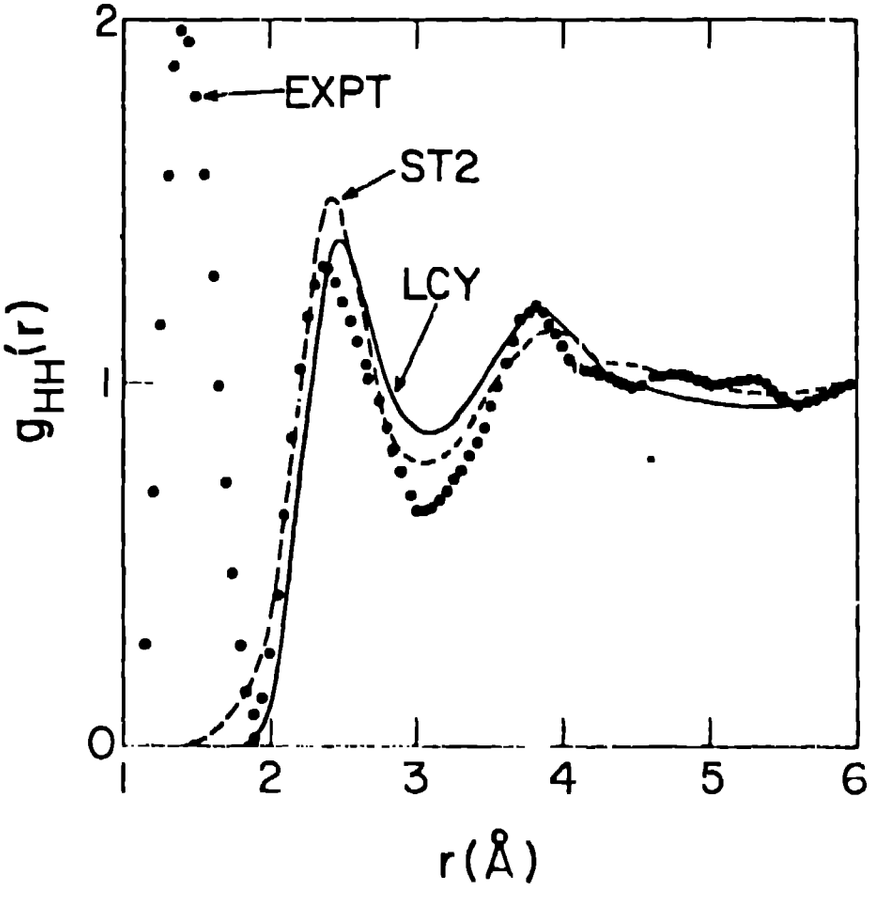


FIGURE 3