Inelastic Neutron Scattering for Materials Sciences and Engineering

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I) INTRODUCTION

The neutron is the ideal probe for studying the positions and motions of atoms in condensed matter⁽¹⁾. Figure 1 shows the region in momentum and energy space the neutron can probe⁽²⁾. Also shown in this figure are scientific areas of condensed matter where neutron scattering provides unique information. These include several areas of interest to materials scientist and engineers.

Figure 1. Energy and momentum space probed by the neutron. The area enclosed in the box is accessible to triple axis instruments. (from ref. 2).

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The main advantage of the neutron in inelastic scattering results from its heavy mass when compared to other particles which are used to probe materials such as the photon (light, x-rays, or γ -rays) or the electron. This means that for a de-Broglie wavelength of $1\text{\AA}^{-1}$, the neutron energy is 82 meV ($1\text{meV} = 0.242\text{ THz} = 8\text{ cm}^{-1} = 11.6\text{ K}$) compared to energies of 120keV for x-rays and 150eV for electrons. Since energies of atomic vibrations in materials are typically about 10 meV, an instrumental energy resolution of $\Delta E/E \sim 10\%$ is needed for neutrons that is easily achievable with existing instrumentation. In order to measure the same energies using x-rays, a resolution, $\Delta E/E \sim 10^{-9}$ is necessary. This resolution is not yet obtainable, but with the arrival of synchrotron radiation x-ray sources it will be achievable in the near future.

The basic laws of conservation of energy and momentum govern the neutron scattering experiment. In an inelastic neutron scattering experiment one measures an intensity^(1,3):

$$I(\mathbf{Q}, \omega) \sim \frac{d^2\sigma}{d\Omega d\omega} = b^2 \frac{k_f}{k_i} S(\mathbf{Q}, \omega) \quad (1)$$

b is the scattering length characteristic of specific atoms and k_i (k_f) is the incident (final) neutron wavevector. The scattering function $S(\mathbf{Q}, \omega)$ is related to the imaginary part of a dynamical susceptibility which is the response of a system to some field:

$$S(\mathbf{Q}, \omega) = (n(\omega) + 1) \chi''(\mathbf{Q}, \omega) \quad (2)$$

$n(\omega) + 1$ is the detailed balance factor that has the following limits:

$$\begin{aligned} n(\omega) + 1 &\sim T/\omega && \text{for } kT \gg \hbar\omega \\ n(\omega) + 1 &\sim 1 && \text{for } kT \ll \hbar\omega \end{aligned} \quad (3)$$

$\chi''(\mathbf{Q}, \omega)$ is the dynamical susceptibility and contains all of the details of the interactions of the system⁽³⁾. It can be written as

$$\chi''(\mathbf{q}, \omega) = FT \langle \rho(\mathbf{i}, 0) \rho(\mathbf{j}, t) \rangle \quad (4)$$

where FT denotes the time and space Fourier transform and $\langle \dots \rangle$ is a correlation function. All of the science of interest is contained in this quantity. ρ can be either a spin or a displacement operator of an atom at position i and time 0 with another atom at position j and time t . If $i \neq j$, we are dealing with correlations among different atoms and coherent scattering is measured. If $i = j$, the time correlations of the same particle is measured, and this self correlation function results in incoherent scattering.

The dynamical susceptibility can be parametrized by:

$$\chi''(\mathbf{Q}, \omega) = \chi''_0(\mathbf{Q}) F(\mathbf{Q}, \omega) \quad (5)$$

where χ''_0 contains the material parameters and $F(\mathbf{Q}, \omega)$ is a normalized spectral shape function. If there is a peak at a finite energy $\omega_0(\mathbf{Q})$, a Lorentzian function with poles at $\omega_0(\mathbf{Q})$ and width $\Gamma(\mathbf{Q})$ will represent the data. In many cases, no "peaks" are observed at finite energy, but a broadening around $\omega \sim 0$ is observed and the spectral shape is a Lorentzian centered at $\omega = 0$, but with a $\mathbf{Q}$ dependent line-width $\Gamma(\mathbf{Q})$. This is usually referred to as quasielastic scattering.

Inelastic scattering of neutrons can be measured using a steady state source such as a reactor, or a pulsed spallation neutron source where there is a well defined time structure⁽⁴⁾. The most versatile instrument used at a reactor is a triple axis spectrometer (TAS) which contains a monochromator and analyzer crystal to define the incident neutron wavevector and energy (k_i, E_i) and the final neutron wavevector and energy (k_f, E_f)⁽⁵⁾. In another instrument, the time-of-flight spectrometer (TOF), the scattered neutrons are energy analyzed by measuring the time they take to reach the detector after striking the sample. This time is inversely related to their energy. In the TAS any point in the four dimensional momentum, energy space of the sample can be measured which is important when dealing with single crystals. If the magnitude, but not the direction, of $\mathbf{Q}$ is of primary importance the TOF instrument may be more suitable. These instruments offer the advantage that many counters can be located around the sample and many $\mathbf{Q}$ -values can be collected simultaneously. The TOF instruments can be located at a reactor or a pulsed source. Because of the inherent time structure of a pulsed source, the TOF technique is ideally suited. The energy transfers probed with a TAS

range up to ~50 meV whereas at a pulsed source energy transfers of 1-2eV are achievable.

Below I shall discuss three examples where inelastic scattering has played a fundamental role in understanding some materials that are important in materials science and engineering.

II) HARD MAGNETS

The first area of interest is that of hard magnets⁽⁶⁾. These materials were developed, in part, by the needs of the automobile industry. In the average automobile there are many places where magnets are needed such as starter motors, windshield wipers, tape drives, speakers, power windows and locks, etc. If stronger magnets can be made, the motors can be reduced in size with a reduction of weight and costs resulting in increased fuel economy and a substantial saving by the manufacturer. General Motors was the leader in the development of the $R_2Fe_{14}B$ magnets where R is a rare earth atom⁽⁶⁾. Neutrons have played an invaluable role in determining the crystallographic structure and the magnetic ordering in these materials as well as characterizing the magnetic interactions leading to the large field strengths. Both magnetic species, the rare earths and the irons, exhibit magnetic order in these materials. There is a strong Fe-Fe interaction resulting in a large molecular field acting on the rare earth ions described by a R-Fe interaction. There is little R-R interaction so the forces on an individual R ion are representative of all rare earth atoms.

Inelastic neutron scattering has been performed on a number of $R_2Fe_{14}B$ samples with various rare-earth atoms^(7,8). The experiments used the TOF method at both a reactor and a spallation sources. Figure 2a shows the inelastic spectrum for $Gd_2Fe_{14}B$ measured at the pulsed source facility ISIS⁽⁷⁾. Gd has a half-filled f shell so the total angular momentum $J=0$ and crystal field effects are negligible. In Fig.2a, the hatched area is the background due to phonon and multiphonon processes. The peak at $\hbar\omega=37.5$ meV is attributed to the average molecular field (H_M) at the Gd site and from its position one obtains a value of $2\mu_B H_M/k_B=435$ K (37.5meV) or $H_M=324$ T. This is 15% larger than the value deduced from magnetization measurements. The asymmetric lineshape suggests that the peak consists of a central peak with two shoulders on either side. This structure can arise from

Figure 2: (a) Inelastic neutron spectra of $\text{Gd}_2\text{Fe}_{14}\text{B}$ (ref. 7) and (b) $\text{Ho}_2\text{Fe}_{14}\text{B}$ (ref. 8). The hatched lines represent the background.

a different H_M acting on the two inequivalent sites for the R atoms and gives $H_M = 358$ and 289 T respectively. The ratio agrees well with the Mössbauer measurements but the absolute values obtained by the Mössbauer studies, 302 and 255 T , are inconsistent with the neutron data.

Figure 2b shows the spectra for $\text{Ho}_2\text{Fe}_{14}\text{B}$ ⁽⁸⁾. It consists of a broad peak centered around 8 meV which is resolved into 3 peaks at 6.7 , 8.0 and 9.0 meV when higher resolution is used (see inset). There have been several theoretical models that calculate the crystal field excitation spectra for these magnets⁽⁹⁾. The inelastic neutron measurements are important in confirming the theoretical models of the magnetic interactions. For the case of $\text{Ho}_2\text{Fe}_{14}\text{B}$, three theories predict a single transition at about 7.5 meV which is in disagreement with the observations. The origin of the extra structure may be due to dispersion because of a finite Ho-Ho interactions, or to the differences in the molecular fields of the two inequivalent R-sites. In order to confirm this, additional experiments have to be performed using single crystals on a TAS instrument.

III) SHAPE MEMORY EFFECT.

Many metallic alloys possess the remarkable property of shape memory which have a wide range of technological applications⁽¹⁰⁾. The shape

memory effect (SME) can be described as follows: a metallic alloy is bent into a certain shape at a temperature above the Martensitic transformation temperature. The specimen is then cooled down below the transformation temperature where it is deformed into a new shape. When it is heated above the transformation temperature, the material, almost miraculously, will return to its original shape. This is called thermoelastic behavior. A similar effect can be induced by straining the sample and then releasing the stress, in which case the behavior is called pseudo-elastic. I shall now discuss how inelastic neutron scattering has played a fundamental role in understanding the macroscopic stress-strain curves in a metallic alloy exhibiting the SME

$\text{Ni}_x\text{Al}_{1-x}$ is an important metallic alloy that is widely used because of its favorable high temperature properties⁽¹¹⁾. In the range of compositions $38 < x < 68$ at % Ni the high temperature structure is the simple CsCl-type structure with Ni atoms at the corner of the cube and Al and excess Ni distributed in the cubic centered positions. For the compositions in the 60-68at% range a reversible martensitic transformation occurs at low temperature.

The lattice dynamics of this alloy has been extensively studied using inelastic neutron scattering and revealed a low lying transverse acoustic branch, propagating along the [110] direction⁽¹²⁾. The atomic displacements associated with this lattice mode corresponds to a shearing of {110} planes along $\langle 1\bar{1}0 \rangle$ directions. The low energy of this mode implies that the coupling between these planes is weak and it takes little energy for these planes to slide relative to one another. The structure of the low temperature martensite phase is a result of different stackings of the {110} planes. Figure 3. shows the low energy region of the dispersion curve of this branch for the $x=62.5$ alloy which transforms at $T_M=85$ K. The anomalous feature is the 'kink' in the dispersion curve which becomes more pronounced as T approaches T_M . A minimum is present near $\zeta \sim 1/7$ which is a precursor to the low temperature 7M structure. This structure corresponds to a 7-fold increase in the unit cell size along the [110] direction⁽¹³⁾.

A recent study by Ye et al⁽¹⁴⁾ calculated the effect of the phonon anomalies on the shear response of NiAl. They found that the anomalous phonon dispersion curve of Fig. 3 is closely connected with the pseudoelastic and thermoelastic behavior of the crystal above T_M . Their results indicated that the anomalous elastic behavior of the SME is an intrinsic property of the

Figure 3: The phonon dispersion curves for [110]-TA mode in $\text{Ni}_{62.5}\text{Al}_{37.5}$ measured at three different temperatures (from ref. 12).

parent crystal as opposed to usual materials in the which the mechanical properties are determined by dislocations and defects. Ye et. al represented the total energy of the crystal as a sum of effective interactions between individual (110) planes:

$$E = - \sum_{n, p \neq 0} W_p \cos[2\pi/b(X_n - X_{n-p})] \quad (6)$$

Here, $(X_n - X_{n-p})$ measures the relative shear displacements in the $\langle 1\bar{1}0 \rangle$ of the n th and $(n-p)$ th (110) planes and b is the distance by which the system repeats itself. W_p is the interplanar coupling constant and is determined by fitting the dispersion curve of Fig. 3 to a Fourier series. The stress-strain behavior is calculated numerically by imposing a small displacement on the boundary layers and letting the other layers relax until the equilibrium is achieved. The displacements of the boundary layers (strain), the forces at the

boundary layers required to maintain the strain (stress), the energy and the configuration are recorded. The process is repeated and the stress-strain curves of Fig. 4 are generated for the three temperatures that the phonon dispersion curve was measured⁽¹⁴⁾. All curves have the stress initially increasing nearly linearly with strain. When the stress reaches a critical value σ_u the system segregates into two phases, the phase with the higher strain is the transformed phase. For sufficiently large stress, the system is completely transformed and the stress increases again with strain. On unloading, the stress-strain curve changes with temperature. For the higher temperatures the system returns completely to its initial state even though it was strained beyond the elastic limit, revealing the

Figure 4: Calculated stress-strain relationships at three different temperatures. Circles and crosses correspond to loading and unloading, respectively. (ref. 14).

pseudo-elastic behavior. For $T=85\text{K}$ a finite residual strain remains when the stress is released. The calculations show that upon heating the system to higher temperatures complete strain recovery is achieved (thermoelastic behavior). The stress-strain curves from this simple model, where the interplanar forces are obtained from the dispersion curve, reproduce all the detailed features observed in experimental stress-loading measurements for many martensitic materials exhibiting the SME.

IV HYDROGEN IN METALS:

The spin incoherent scattering cross section is related to the interaction of the magnetic moment of the neutron with the nuclear spin. For the case of hydrogen with nuclear spin $1/2$, the incoherent cross section is nearly 80 barns, which is the largest scatterer of all elements^(3,15). It is over an order of magnitude larger than most coherent scatterers. This has been used advantageously over the years in studying hydrogen motion in solids. The incoherent scattering probes the self-correlation function:

$$S_{\text{inc}}(Q, \omega) \sim \text{FT} \langle \rho(i, 0) \rho(i, t) \rangle \quad (7)$$

which is the time dependent motion of a single particle, in this case the hydrogen atom. Typical applications have been the study of hydrogen motion in polymers, organic materials and biological systems. Below I shall discuss how inelastic neutron scattering has been used to study hydrogen motion in metallic hydrides. This subject is technologically important because of their use as energy storage devices, fusion technology and understanding hydrogen embrittlement. Particularly, I shall emphasize studies of hydrogen diffusion in transition metals and studies of local modes which gives information about the hydrogen potential.

The simplest model for diffusional motion is the single jump model (Chudley-Elliott model) where the diffusion occurs over well localized sites interconnected by a set of jump vectors, S_k . The mean resident time, τ , is assumed to be long compared to the jump time. The jump probability to any of n adjacent sites is $1/n\tau$. Other assumptions in this model are that the jumps and oscillations are uncorrelated and that the concentration of hydrogen is so small that there are no interaction effects. The diffusing

hydrogen atoms cause an energy broadening of the scattered neutrons which can be characterized as a Lorentzian centered around zero energy transfer. The observed intensity is proportional to:

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{\Gamma(\mathbf{Q})}{\omega^2 + \Gamma(\mathbf{Q})^2} \quad (8)$$

where $\Gamma(\mathbf{Q})$ is the half width at half maximum and contains information about the jump distance and time:

$$\Gamma(\mathbf{Q}) = \frac{1}{n\tau} \sum_{k=1}^n [1 - \exp(-i\mathbf{Q} \cdot \mathbf{S}_k)] \quad (9)$$

It can be seen that the linewidth will vary with $\mathbf{Q}$, and when $\mathbf{Q}$ approaches the jump vector it will approach zero. For small $\mathbf{Q}$:

$$\Gamma(\mathbf{Q}) = 2DQ^2 \quad (10)$$

where D is the self-diffusion constant.

$\Gamma(\mathbf{Q})$ depends upon the direction and the symmetry of the jump site. This has been used extensively in the study of hydrides to determine the local symmetry and the jump site of the hydrogens⁽¹⁶⁾. Figure (5) shows the behavior of $\Gamma(\mathbf{Q})$ in $\text{PdH}_{0.03}$ measured along the [100] and [110] direction⁽¹⁷⁾. $\text{PdH}_{0.03}$ has an FCC symmetry and the H can occupy either tetrahedral or octahedral sites. Using eq. (9) for $\mathbf{Q} \parallel [100]$ gives identical results for octahedral or tetrahedral sites. On the other hand for $\mathbf{Q} \parallel [110]$ the linewidth behaves differently for the two site occupancies. From this data it is confirmed the H in $\text{PdH}_{0.03}$ diffuses amongst the octahedral sites.

For BCC transition elements such as tantalum the simple model cannot describe the hydrogen diffusion⁽¹⁸⁾ as shown in Fig (6) where $\Gamma(\mathbf{Q})$ is plotted as a function of rotation of the sample for $|\mathbf{Q}| = 2.0 \text{ \AA}^{-1}$. The linewidth is nearly constant at 1 THz which differs from the predictions of the simple jump diffusion model for both tetrahedral and octahedral jump sites. Since the hydrogens are believed to occupy tetrahedral sites a more complicated model for the hydrogen diffusion is required.

Figure 5: Incoherent quasielastic linewidth in $\text{PdH}_{0.03}$ measured along the [100] and [110] direction. The lines are model fits from Eq. (9). (ref. 17)

Figure 6: Incoherent quasielastic linewidth for the BCC hydride $\text{TaH}_{0.02}$ as function of orientation for a constant $|Q| = 2.0 \text{ \AA}^{-1}$. The lines are model fits with eq. (9).

Another application of inelastic incoherent neutron scattering in the study of hydrides is high energy vibrational spectroscopy where direct information about the hydrogen single particle potential. The experiments were performed on a single and multi-domain single crystal of β -V₂H at a pulsed spallation source at low temperature⁽¹⁹⁾. Figure 7 shows the inelastic spectrum measured on a multidomain sample. The inset shows the higher energy region measured on the single domain crystal. Peaks are observed all the way up to nearly 1.5eV. The indices below these peaks correspond to the vibrational directions as determined on the single domain sample. The most intense peaks are the fundamental vibrations with displacements along [100] and [010] near 50 meV (not resolved) and along [001] near 220 meV.

Figure 7: Incoherent inelastic neutron spectra for β -V₂H. The (hmn) indices indicate the various transitions associated with hydrogen vibrations along (xyz). (Ref. 19)

The excitation energy is plotted as a function of excitation number, n , in Fig. (8). For the stiff [001] direction the excitation energies are linear with quantum number which implies a very harmonic potential. In the soft [100] direction, the higher energy levels are practically equidistant, but at lower energies the spacing is closer together implying an anharmonicity consistent

with a flattened bottom. The assumed potential that describes the spacing is the sum of a parabola and a gaussian giving the resulting potential well

Figure 8: Left side: Hydrogen excitation energies vs quantum numbers for: (+) the stiff (001) direction and (o) the soft (100) direction. Right side: the hydrogen potential in the soft (100) direction and the corresponding energy levels. (Ref. 19)

shown on the right side of the figure. The harmonic excitation energies are calculated from this well are 104meV, 107meV, and 223 meV for the [100], [010], and [001] directions, respectively⁽¹⁹⁾. For the soft direction the potential is relatively flat over a range of about 6 Å. Based on the inelastic neutron results one now has a detailed picture of the hydrogen diffusion and potential in the transition metal hydrides.

V. CONCLUSIONS

Inelastic neutron scattering is a powerful tool for studying microscopic motions in a solid. The information obtained from these measurements is very important in characterizing and understanding materials that have a technological interest such as metallic alloys, magnet materials and many hydrogen containing substances such as hydrides, polymers and biological samples.

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