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## DISCLAIMER





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## ABSTRACT

A brief review of Brillouin scattering is made emphasizing its advantages and disadvantages over conventional ultrasonic techniques. One of its advantages is that the elastic properties of very thin films (~1 μ) can be investigated. We have used this technique to study changes in shear elastic constants of materials irradiated with high energy ions. These particles only penetrate ~1μ into the material but produce very high defect concentrations which, in certain cases, can lead to amorphization. In $Nb_3Ir$ and $Zr_3Al$ very large changes are observed before the onset of amorphization, while in Si the changes occur concomitantly with amorphization. The significance of the hardening observed in $Zr_3Al$ when it becomes amorphous will be discussed.

Brillouin scattering--which is the scattering of light by acoustic phonons[1]--is an alternative to ultrasonic techniques commonly used for the determination of the elastic properties of materials. It is true that Brillouin scattering suffers from many drawbacks; it is less accurate than ultrasonics, attenuation measurements are extremely difficult, transparent materials are usually required and the refractive index usually enters into the data analysis. On the other hand, it has certain advantages; it can deal with extremely small samples ($\sim 10^{-6}$ g of helium, Ref. 2), it can be used to study materials under extreme conditions of temperature and pressure (1550 K in Ref. 3 and 700 kbar in Ref. 4), and to study highly reactive or fragile samples where the bonding of transducers is non-trivial (e.g., the shear constant of graphite in Ref. 5).

When dealing with nontransparent materials, the disadvantages of Brillouin scattering are even greater. In these cases light couples only to surface waves and hence information on only a few of the elements of the elastic constant tensor can be obtained. In most cases the same information can be obtained (more accurately) by using ultrasonic Surface Acoustic Wave (SAW) technology. Before describing cases where Brillouin scattering has certain advantages, we briefly review the basic concepts of surface waves, a complete description can be found in Ref. 6.

Surface waves arise as a solution to the equations of motion when the boundary conditions are changed from an infinite medium to a medium bounded by a surface. If the free surface is at $z=0$ then the solutions to the wave equation must satisfy $\sigma_{iz}=0$ $(i=x,y,z)$ where $\sigma$ is the stress tensor. In general, the solution is of the form

$$\vec{\mu} = \vec{\mu}_o \, e^{i(\vec{q}_\parallel \cdot \vec{r} + \omega t)} \, e^{-\alpha z} \qquad (1)$$

where $\vec{\mu}$ is the displacement at a position $\vec{r}$ and at a time t, $\omega$ is the frequency, $\vec{q}_\parallel$ the wavevector parallel to the surface and $\alpha$ is a measure of the amplitude attenuation away from the free surface. Typically $\alpha \approx q_\parallel$ which indicates that the amplitude decays over a distance roughly equal to the wavelength of the phonon. The velocity (v) of this surface excitation can be written as

$$v = \omega/q_\parallel = \beta \, v_T \qquad (2)$$

where $v_T$ is the velocity of the bulk (infinite medium) transverse mode which is polarized perpendicular to the surface, and $\beta$ a number which is a slowly varying function of the elastic moduli ($C_{ij}$). In all but the simplest cases analytical expressions for $\beta$ are not available and numerical calculations are required; typical values for $\beta$ are $0.90 \pm 0.05$.

From the above comments it is clear that the study of surface waves to determine specific elastic constants is extremely difficult. However, it does have the advantage that it can be applied to materials that can only be prepared as thin films. Since the amplitude of the wave decays over approximately one wavelength, Brillouin scattering is even more attractive than conventional SAW technology because it allows thinner films to be investigated. Typical wavelengths which can be achieved in SAW experiments are tens of microns, the study of any film thinner than this therefore requires elaborate, and often uncertain, corrections for the effect of the substrate. Brillouin scattering allows films down to ~5000 Å thickness to be investigated without interference from the substrate, and, for example, has proved to be a valuable

tool in the study of the elastic properties of metallic superlattices.[7]

Here the results of investigations probing the elastic properties of materials subjected to ion irradiation will be presented. These studies allow the effects of extremely high defect concentrations produced by ion bombardment (which in some cases lead to amorphization) to be investigated. Since ions in the MeV energy range only penetrate $\lesssim 1\ \mu$, Brillouin scattering is eminently well suited for the task. It should be pointed out that other bombardment techniques, (viz., neutrons and electrons) which have larger penetration depths can produce samples large enough for ultrasonic experiments, however years of irradiation times are required to produce the same defect concentrations that can be generated in a few hours by ion beams. Brillouin scattering studies of ion irradiated samples has the additional advantage that most of the ions stop at a depth outside the range probed, and hence an analysis can be made based only on regular defects (vacancies, interstitials and anti-site) and not the addition of impurity atoms.

Figure 1 shows the surface wave velocity in $Nb_3Ir$ irradiated with 1.8 MeV $\alpha$-particles.[8] (The insert is for irradiation with 250 keV protons.) In spite of the fact that these samples remained crystalline even at the highest doses there is a dramatic change in the sound velocity which corresponds to a 40% change in a shear elastic constant.

Figure 2 shows similar results for $Zr_3Al$ irradiated with 1 MeV Kr ions.[9] Here again a large softening is observed in the region where the sample is still crystalline (below doses of $5\times10^{13}$ Kr/cm$^2$). A more unexpected effect is observed just above this dose where the velocity increases over the same region where electron microscopy shows signs that part of the material has become amorphous. This result is perhaps the first clear evidence that amorphization by irradiation is not a continuous process but more like a phase

transition (first order?) from a highly defected crystal to the amorphous state. Detailed comparisons of the Brillouin results with those of electron microscopy are given elsewhere,[9,10] but they show that our results support a theory of amorphization which is similar to that of melting.[11,12] In this picture the ion dose is equivalent to the amount of "heat" in a crystal: as heat (dose) is added the lattice expands and the elastic constants decrease (both observed experimentally[10]), further heat (dose) can produce a superheated crystal which at some point phase-separates into a crystal, with a slight lattice contraction, and a liquid (amorphous) phase. This coincides with the experimentally observed lattice contraction,[10] increase in sound velocity, and the appearance of two phases.[9,10] Further heat (dose) slowly converts the remaining crystal into a liquid (amorphous solid) with no change in lattice spacing, also as observed experimentally.

We return now to the softening observed in the region where the sample is crystalline. It can be shown[10] that the elastic constants of a crystal with anti-site disorder can be written in the form

$$C = C_1 + C_2 S^2 \tag{3}$$

where S is the Bragg-Williams long range order parameter equal to 1 in the fully ordered state and 0 in the fully disordered state. Using the ion-dose dependence of S determined from electron diffraction patterns and taking $C_1$ and $C_2$ as fitting parameters, Eq. 3 yields an excellent fit to our data on both $Nb_3Ir$ and $Zr_3Al$.

An alternative approach[8] which was used to explain the results of $Nb_3Ir$, is based on the electronic contribution to the elastic constants. There it was found that the softening could be explained by the changes in the

electronic density of states at the Fermi energy produced by the irradiation. (The change in the density of states was derived from changes in the superconducting transition temperature.)

The two approaches mentioned above may be equivalent since it has been shown[13] that the changes in electronic properties with the state of order can be described in terms of effective pairwise interactions. It turns out that the internal energy is a quadratic function of the long-range order parameter, S, exactly as in the Bragg-Williams approximation used in deriving Eq. 3.

Preliminary experiments on Si show no softening before the onset of amorphization, unfortunately this does not help to distinguish between the two proposed mechanisms since Si has no "anti-sites" but neither does it have an appreciable contribution to the elastic constants from the conduction electrons.

Further work is obviously required in order to fully understand the process of amorphization, and the elastic behavior during damage. Hopefully the combination of Brillouin scattering and electron microscopy will provide us with valuable insight into the mechanisms involved.

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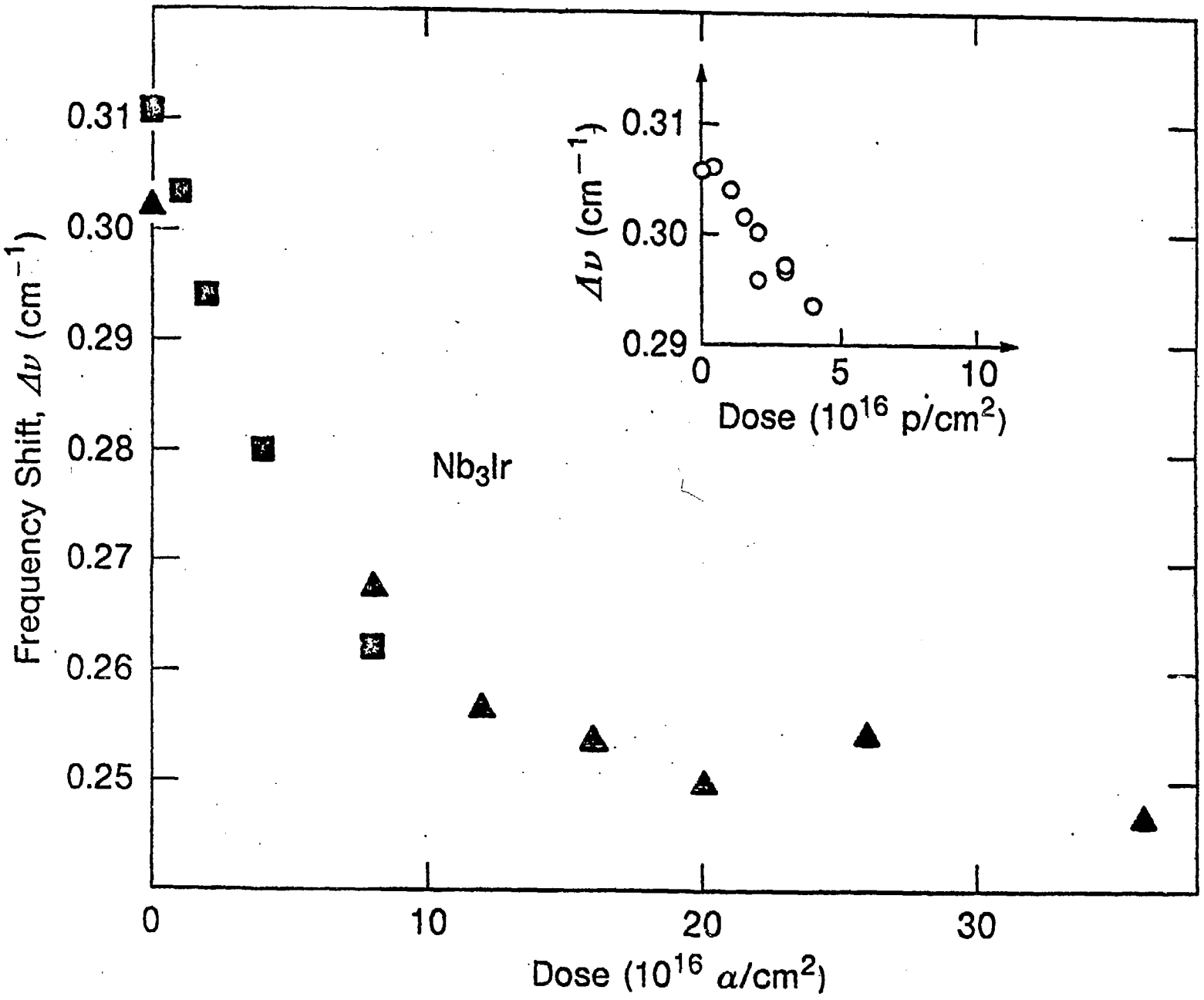
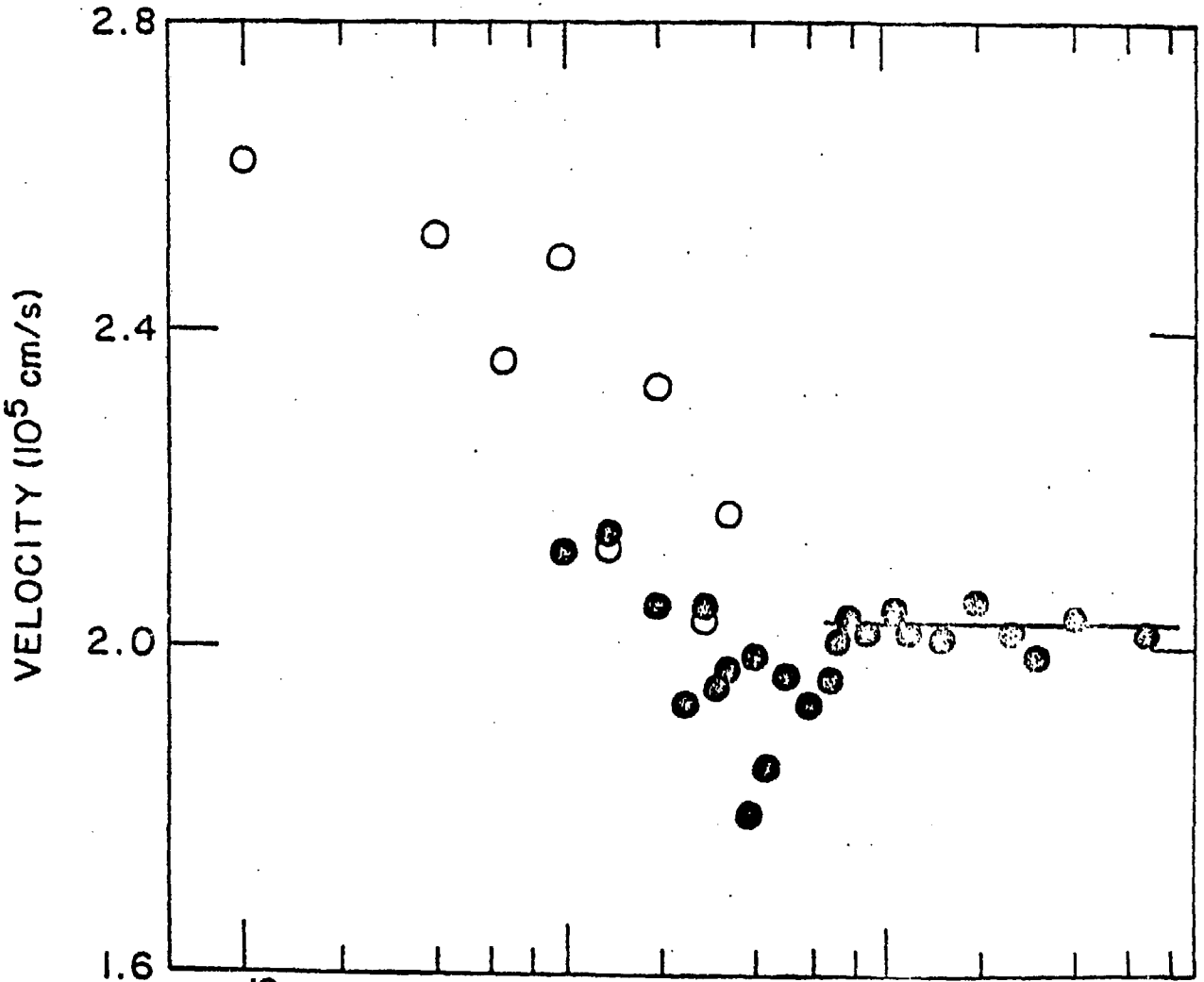
## FIGURE CAPTIONS

Fig. 1. The Brillouin frequency shift (proportional to sound velocity) vs. dose of α-particles in $Nb_3Ir$. The insert is for irradiation with protons.

Fig. 2. Sound velocity in $Zr_3Al$ as a function of Kr ion dose. Open and filled circles denote respectively broad and narrow peaks in the Brillouin spectra.


0.31
0.30
0.29
0.28
0.27
0.26
0.25
Frequency Shift, Δν (cm⁻¹)
Nb3Ir
0
10
20
30
Dose (10¹⁶ α/cm²)
Δν (cm⁻¹)
0.31
0.30
0.29
0
5
10
Dose (10¹⁶ p/cm²)


2.8
2.4
2.0
1.6
VELOCITY ($10^5$ cm/s)
$10^{12}$
$10^{13}$
$10^{14}$
DOSE (Ions/cm$^2$)