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Brillouin scattering study of lattice-stiffness changes due to ion irradiation: Dramatic softening in Nb_3Ir

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We demonstrate a novel approach for studying progressive disorder which couples the versatility of charged-particle irradiation with subsequent measurements of elastic properties using Brillouin scattering. Irradiated films of Nb_3Ir, which remain crystalline, show a dramatic reduction in an average shear elastic constant of up to 40%. The large softening of this long-wavelength shear mode is difficult to explain with the conventional resonant-mode defect model used in simple metals and alloys. However, in qualitative agreement with existing theoretical models, the softening shows a strong correlation with the measured electronic density of states at E_F, which changes significantly with irradiation dose.

We present a technique for studying progressive disorder (which could eventually lead to amorphization) that couples the versatility of charged-particle irradiation with subsequent measurements of elastic properties using Brillouin scattering from surface waves. This technique probes depths of ~ 0.5 μm from the surface. Since the irradiated layer is typically $\gtrsim 1$ μm thick, and quite uniform near the surface, the results are obtained without interference from the substrate. Our results on Nb_3Ir, which span a region of damage in which the sample retains its crystallinity, show a surprisingly large drop of $\sim 40\%$ in a shear elastic modulus.

Such an enormous net change in a shear elastic constant is hard to account for with the conventional explanation of resonant defect modes used in the theory of irradiated simple metals.[1] Instead, following the elasticity theory of metals, we propose that for the case of Nb_3Ir, the softening is chiefly due to changes in the electronic density of states at the Fermi energy $N(E_F)$. A strong correlation is found to exist between the elastic modulus and $N(E_F)$, which is determined from the superconducting transitions of the irradiated samples.

Extensive literature exists on the effects of irradiation on the elastic properties of materials.[1-18] Most of this work, however, pertains to relatively low defect concentrations because conventional elasticity measurements require relatively large sample sizes. This requirement has, to a large degree, restricted elastic measurements to samples irradiated by either neutrons[2-11] or high-energy electrons[12-15] that have large penetration depths, but produce lower defect concentrations. The very high defect concentrations which are achievable with ions have not been so widely investigated since they require the use of nonconventional techniques.[16-20]

Because Brillouin scattering from surface waves probes a region smaller than typical ion penetration depths, no corrections are needed for the undamaged part of the sample. The advantages of this are clearly evidenced by comparing the data analysis of the elastic properties of amorphous Si which were probed by vibrating-reed[19] and Brillouin scattering[20] techniques.

The Brillouin scattering experiments were carried out using a tandem Fabry-Perot interferometer[21] with ~ 200 mW of 5145-Å radiation from a single-mode Ar laser. All measurements were done at room temperature. As is the case for all Brillouin scattering measurements from metals, essentially only scattering from surface waves is observed.[21] These waves propagate along the surface of a material and their amplitude decreases exponentially away from the surface. The velocity of surface waves is closely related to the velocity of shear modes in the bulk. In our case of a polycrystalline sample, this bulk velocity will result from some weighted average of the elastic constants c_{44} and $(c_{11}-c_{12})/2$. However, since we find no appreciable anisotropy for surface wave velocities measured in the (111) plane of a Nb_3Ir single crystal, and since these values are almost identical to our undamaged polycrystal films, it can be assumed that the elastic anisotropy is small, i.e., $2c_{44} \approx c_{11}-c_{12}$.

Our samples, polycrystalline Nb_3Ir films (~ 0.5 μm thick) were deposited on sapphire substrates and irradiated at somewhat elevated temperatures with 0.25-MeV protons or 1.8-MeV α particles; they are described in more detail in Ref. 22. From x-ray measurements, we know that our samples remain crystalline, since well-defined Bragg peaks are observed even at the highest doses. The lattice constant is found to expand slightly ($< 1\%$) at the larger doses.

In Fig. 1 we present our measurements of the Brillouin frequency shift, $\Delta\nu$, as a function of the irradiation dose of α particles. The velocity of the surface phonons v_s can be obtained from the data of Fig. 1 by multiplying the frequency shift (in cm^{-1}) by 8.91 to obtain v_s in units of km/sec. A noteworthy feature of Fig. 1, however, is the *magnitude* of the decrease during irradiation, which implies a reduction of $\approx 40\%$ in the elastic shear modulus even before the amorphous state is reached. The measured changes in phonon velocity saturate at high doses, which is consistent with the saturation of the superconducting properties reported in Ref. 22. Saturation is expected, because of the spontaneous recombination of defects at high concentrations. Hence the exponential decay of $\Delta\nu$ with dose (Fig. 1) is consistent with $\Delta\nu$ being proportional to the average concentration of irradiation-induced defects. The

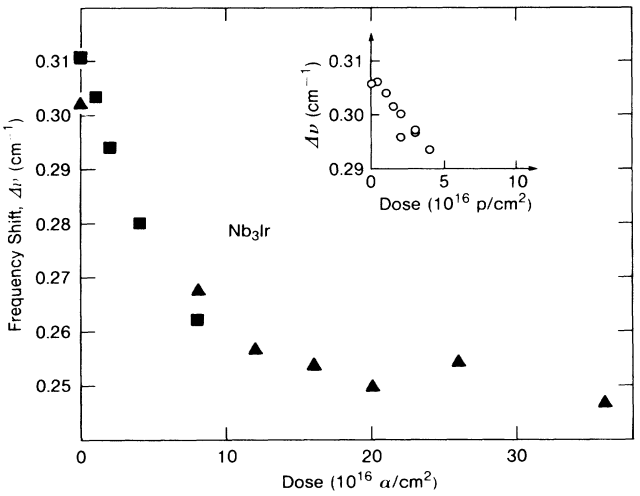

FIG. 1. The frequency shift measured by Brillouin scattering vs dose of α-particle irradiation onto Nb_3Ir sputtered films. Inset: the same data for proton irradiation. The filled triangles and squares correspond to two films of Nb_3Ir with similar properties prior to irradiation, sections of which were irradiated with different doses of α particles.

initial slope of $\Delta\nu$ as a function of Frenkel-pair production is within the range found for other materials (see, for example, Table V in Ref. 9). The Frenkel-pair concentration is determined from calculations of the energy given up in atomic displacements using the TRIM computer code.[23] This same analysis for a 250-keV proton irradiation predicts a factor 2.8 smaller initial slope with the dose in good agreement with the results for protons shown in the inset of Fig. 1. Hence, at least for small doses, the elastic constant changes are directly proportional to the energy deposited into atomic displacements. Measurements of the superconducting transition temperature T_c also show a factor of 2–3 times smaller effect per particle with proton irradiation.[22] The saturation concentration of defects can also be derived from Fig. 1 and is found to be a relatively high value of ≈ 0.07 displacements per atom.

The explanation which has been given for the softening observed in many materials with low defect concentrations is based on the existence of "resonant modes" of three-dimensional interstitial configurations that couple to the phonons in the acoustic band and produce the softening.[24] In the case of Nb_3Ir, the large measured saturation defect concentration implies a defect recombination volume considerably smaller (~ 10 times) than that found in single-element materials.[25] Also, the three-dimensional interstitial configurations that are responsible for low-lying resonant modes are not expected to exist after a room-temperature irradiation to high doses. Thus, considerable doubt exists as to the applicability of the resonant-mode model to explain the large observed velocity changes. Of course, it is possible that antisite defects could cause the softening or stabilize Frenkel pairs in smaller volumes, but relevant studies do not exist.

Instead, we propose here that the observed softening in Nb_3Ir is due mainly to irradiation-induced changes in the electronic structure of the material. It is well known that electronic structure plays a fundamental role in the determination of the elastic constants of metals, many of which can now be calculated from first principles with reasonable accuracy.[26,27] In a systematic review of the elastic constants of metals, Steinemann and Fisher[28] have shown that the elastic constants (c_{ij}) can be written as

$$c_{ij} = c'_{ij} + \int_0^\infty D(E) f(E) N(E) dE - A^2 N(E_F) \ , \quad (1)$$

where c'_{ij} results from the bare-ion interaction screened by the conduction electrons, $D(E)$ is a deformation potential, $f(E)$ is the Fermi-Dirac distribution function, $N(E)$ is the density of states, E_F is the Fermi energy, and A is another deformation-potential constant. The calculations of Ref. 27 for cubic transition metals show that all three terms can play an important role.

In our case of ion-irradiated films, the total number of electrons remains constant, so that variations of the second term in Eq. (1) probably can be ignored, and $N(E_F)$ alone is of interest. Measurements of Pauli susceptibility to obtain $N(E_F)$ would be quite challenging for the very small sample volumes that can be conveniently irradiated. However, the superconducting transition temperature T_c has been measured[22] on these samples and is related to the electron-phonon coupling constant λ which has been shown[29] to be proportional to $N(E_F)$ for $A15$ superconductors like Nb_3Ir.

Thus, in Fig. 2 we have plotted our values of v_s^2 vs λ (since $c_{ij} = v_s^2 \rho$, where ρ is the density which varies negligibly with ion dose), and find a strong correlation, as well as the qualitative decrease predicted by the third term of Eq. (1). The fact that Fig. 2 shows a linear relationship be-

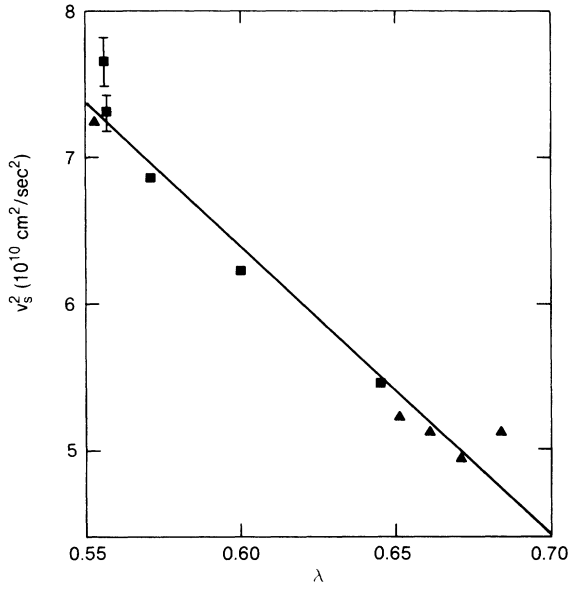

FIG. 2. The variation of v_s^2 (proportional to c_{ij}) as determined from the data of Fig. 1 plotted against the electron-phonon coupling constant λ [proportional to $N(E_F)$] as determined from the data and analysis of Ref. 22. The straight line is a least-squares fit to the data.

tween v_s^2 and λ, in agreement with the third term of Eq. (1), is perhaps fortuitous since there are uncertainties in the determination[22] of λ from T_c which are hard to estimate. Also, the first term in Eq. (1) may play a role. Recall that for longitudinal phonons, the Fermi-Thomas screening of the bare-ion frequencies leads to long-wavelength phonon frequencies which are inversly proportional to $N(E_F)$ in a free-electron model. Although such results cannot be carried over directly to the shear modes studied by Brillouin scattering, it seems reasonable to expect some contribution (e.g., see calculations in Ref. 27).

A more satisfying confirmation that $N(E_F)$ plays an important role would be to demonstrate its effect on materials in which $N(E_F)$ *decreases* with disorder. Although this is the more customary behavior of $A15$ superconductors, we are only aware of one study[4] for which there are measurements of acoustic properties. These data[4] on V_3Si indeed show that T_c decreases with disorder, implying a decreased $N(E_F)$, and that the elastic constants simultaneously increase. Thus these results are also in agreement with our interpretation of the observed softening in Nb_3Ir based on Eq. (1).

A somewhat more indirect confirmation that changes in $N(E_F)$ are important in understanding the elastic properties of metals is work currently in progress on irradiated Si. In Si, $N(E_F)$ is negligible compared to that in a metal, and preliminary measurements reveal no large changes in velocity until the material starts becoming amorphous.[30]

In conclusion, we have shown that Brillouin scattering is a powerful tool for the study of ion-irradiated samples, and we have proposed a mechanism based on changes in the electronic structure—notably the density of states at the Fermi energy—to account for the large elastic softening found in irradiated Nb_3Ir.

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