Observation of Raman Scattering in an Amorphous Metal

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The first observation of Raman scattering is reported for an amorphous metal. An interference-enhancing trilayer configuration is used. Measurements on transition-metal–metalloid alloys of a-$Ni_{0.67}B_{0.33}$ provide information on the form of the weighted phonon density of states of Ni-Ni and Ni-B derived bands and Raman-coupling-parameter variations.

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Raman scattering has been shown to be a valuable means of studying the dynamics of amorphous semiconductors and insulators as well as providing information on structural order and its variations with deposition conditions in the former.[1] These measurements provide important constraints on models of bonding and structure in noncrystalline solids and liquids.[2] However, the important class of noncrystalline metallic systems has not successfully been studied to date, though a number of attempts have been made.[3] In amorphous semiconductors, Raman intensities are often enhanced by electronic resonances near the optical gap, while in insulating glasses the large penetration depths provide for significant scattering volumes. In contrast, amorphous metals are expected to have weaker resonant enhancement, higher reflectance, very small penetration depths, and increased stray-light background. It had been suggested[4] that such measurements were not feasible. In this work we report on the successful observation of Raman scattering from the important class of amorphous binary alloys composed of transition-metal (TM) and metalloid (m) constituents. The results provide information on the weighted vibrational density of states as well as Raman coupling parameters. The vibrational spectra also provide important information on the TM-TM and TM-m interactions. The observation of Raman scattering in amorphous metallic thin films further implies that the vibrational states of a broader class of compositions than conventional splat-cooled systems may also now be studied. In addition, problems relating to variations in structural order with thin-film deposition conditions that parallel amorphous-semiconductor studies[1] are feasible.

The very weak Raman scattering of amorphous metals implies that enhanced scattering or detection methods are required. We have utilized the former approach, by employing the interference-enhanced Raman scattering (IERS) technique[5] in which an increased local field in a trilayer film structure allows an approximate order-of-magnitude increase in signal intensity. This method has previously been utilized to study thin layers of amorphous semiconductors and crystalline intermetallics as well as their changes with annealing due to interfacial reactions[5] or structural ordering.[6] The present trilayer structure consisted of a bottom evaporated Al reflecting layer, an rf-sputtered a-SiO_2 dielectric spacer, and a very thin top layer of the amorphous metal alloy a-$Ni_{0.67}B_{0.33}$. The amorphous metal films were deposited at a sputtering pressure of 8 mTorr of Ar. At these pressures thicker films have been found to yield reduced columnar structure. No studies, such as electron microscopy, were made of the very thin-film layer morphology. However, the stability of the films under atmospheric conditions is qualitatively consistent with a small concentration of voids. The thicknesses employed to achieve the IERS condition of low total reflectance at the laser excitation wavelength were ~650 Å of a-SiO_2 and ~50 Å of amorphous metal alloy. The optical constants of a thick amorphous film were estimated from multiple-angle reflectance measurements. The values were then employed to obtain the desired thicknesses of IERS.[5] Reported here are IERS measurements on an a-$Ni_{0.67}B_{0.33}$ trilayer structure of reflectance less than 0.5% at 5145-Å excitation wavelength. Successful spectra have also been obtained on metallic alloys of a-$Ni_{0.5}B_{0.5}$ and a-$Fe_{0.5}B_{0.5}$. Far-infrared reflectance measurements indicated typically metallic character were Drude-type behavior yielded a resistivity of 192 $\mu\Omega$ cm. This value is comparable to, though larger than, that of a splat-cooled metal foil,[7] 127 $\mu\Omega$ cm. A major experimental difficulty was the observation of luminescence from the a-SiO_2 layer, which necessitated variations in the rf-discharge conditions to reduce defects and improve stoichiometry. A Spex third monochromator system was employed to reduce stray light. The reported horizontal, polarization-unanalyzed Raman spectrum was obtained at ~300 K with a cylindrical lens to minimize heating.

The measured Raman spectrum, I_t, of a-$Ni_{0.67}B_{0.33}$ is shown in Fig. 1(a). The spectrum includes a structureless background contribution from stray light at low frequency as well as high-frequency luminescence. The inelastic Raman contribution is distinguished by two broad bands between ~50 and 800 cm^{-1} associated with features in the phonon density of states which are modified by the appreciable background. The lower curve in Fig. 1(a) indicates the estimated normalized stray-light background obtained from an adjacent bilayer film of Al and a-SiO_2. As the Raman scattering of the latter is very weak for the thickness employed, this provides a useful means of obtaining a good first-order approximation to the form of the stray-light scattering due to surface roughness. The resulting inelastic spectrum in Fig. 1(b), obtained after smoothing, indicates the presence at high frequencies of a monotonically increasing background due to SiO_2 luminescence, as also observed in some thick bilayer SiO_2/Al structures. Higher-frequency measurements indicate that this has an approximately linear tail, which can be extrapolated, as denoted by the dashed curve of Fig. 1(b), to allow reasonable subtraction of its contribution. A subtraction of the stray-light and luminescence backgrounds along with a smoothing yields the Raman intensity shown in Fig. 1(c). The importance of these background subtractions is indicated by the significant shift of the low-frequency peak between Figs. 1(a) and 1(c), from 97 to 138 cm^{-1}. This is a consequence of the appreciable relative stray-light contribution in amorphous metal films. As the luminescence extrapolates to its required zero intensity at $\omega = 0$, this implies that the background estimates are reasonable. The detailed form of the luminescence does not, however, influence substantially the resulting Raman spectrum given this constraint.

As crystal momentum is not a conserved quantity in amorphous solids, the Raman intensity of Fig. 1(c) is related to the phonon density of states $g(\omega)$ for Stokes scattering by the approximate equation $I_R(\omega) \sim \tilde{C}(\omega)\omega^{-1}(n+1)g(\omega)$. The quantity $\tilde{C}(\omega)$ is an average frequency-dependent coupling parameter appropriate to the scattering configuration.[1] In amorphous solids $\tilde{C}(\omega) \sim \omega^2$ in the very-low-frequency Debye-type regime.[8] The low-frequency peak in Fig. 1(c) at ~ 138 cm^{-1} is primarily associated with contributions to the phonon density of states of Ni-Ni vibrations. This identification is based on theoretical studies[9] of Ishii and Fujiwara of the partial density of states of a-$Fe_{1-x}P_x$ alloys which indicate a dominant Fe-Fe and a small structureless metalloid contribution in this spectral range. Although theoretical Raman studies have not been performed for amorphous metal alloys, the low-frequency transition-metal-derived peak may be compared to theoretical Raman[10] and $g(\omega)$ calculations[10–12] of pure a-Ni or a-Fe. These studies indicate a broad low-frequency band with subsidiary structure that parallels the distinct transverse and longitudinal acoustic bands of crystalline Ni. However, this subsidiary structure in a-Ni is sensitive to disorder.[12] As such, the absence of two distinct features in the low-frequency spectral band of Fig. 1(c) may be due to additional structural or compositional disorder in the alloy thin film. Additional Raman studies on more dilute alloys are in progress to explore this issue as well as polarization effects predicted in the Raman theory.[10]

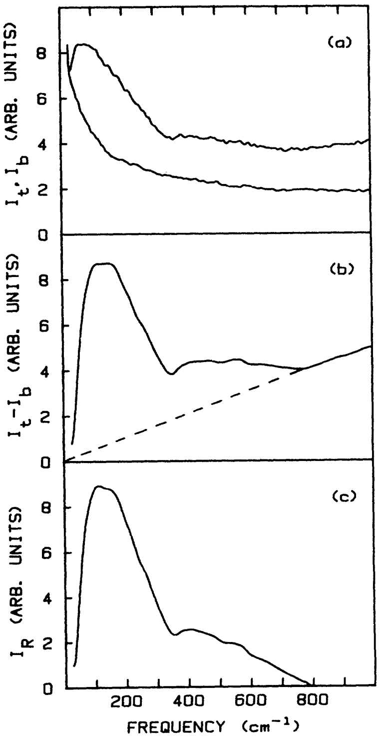

FIG. 1. (a) Total Stokes intensity, I_t, of an a-$Ni_{0.67}B_{0.33}$ trilayer and its stray-light background, I_b; (b) $I_t - I_b$ after smoothing, and extrapolated luminescence (dashed line); and (c) Raman intensity.

At higher frequencies Fig. 1(c) indicates a weaker band with a peak at 415 cm^{-1} and a shoulder at ~ 570 cm^{-1} as well as a tail extending to ~ 800 cm^{-1}. This band is associated with Ni and B motions. Previous inelastic neutron scattering[13] and theoretical studies[9] of a-$Fe_{0.78}P_{0.22}$ imply that this opticlike band has contributions from Fe and P motions. In a-$Ni_{0.67}B_{0.33}$ the considerably lighter B metalloid results in a shift of this band to higher frequencies relative to the predominantly transition-metal-determined band at lower frequencies. As such, the high-frequency band is expected to have a larger metalloid contribution than in a-$Fe_{0.78}P_{0.22}$. This implies that this optic band has a more cagelike character in which the B atom moves in a Ni cage of $\sim$8–9 atoms.[14] The overlap of the low- and high-frequency bands in Fig. 1(c) implies, however, that an isolated local cagelike band does not occur and that the phonon eigenvectors involve both TM- and m-atom displacements.

Preliminary inelastic-neutron-scattering measurements[15] in splat-cooled foils of a-$Ni_{0.67}B_{0.33}$ indicate that the low-frequency Ni-Ni peak occurs at 182 cm^{-1}. As the neutron spectra are related to the weighted partial densities of states of TM and metalloid atoms, they yield essentially the Ni-Ni low-energy peak in $g(\omega)$. The frequency shift of 44 cm^{-1} between the Raman peak of Fig. 1(c) and the neutron results is thus due to the frequency dependence of $\tilde{C}(\omega)$. Figure 2 compares this measured Raman spectrum to that obtained by dividing the spectrum by the factors $n+1$ and $(n+1)/\omega$. These correspond to estimating the density of states from $I(\omega)$ under

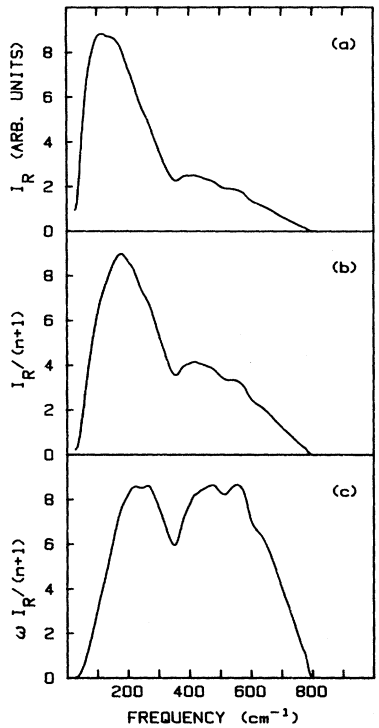

FIG. 2. (a) Smoothed horizontal, polarization-unanalyzed Raman spectrum $I_R(\omega)$ of a-$Ni_{0.67}B_{0.33}$ after background subtractions; (b) $I_R(\omega)/(n+1)$; and (c) $\omega I_R(\omega)/(n+1)$.

the simplified conditions associated with a linear variation of $\tilde{C}(\omega)$ and a constant $\tilde{C}(\omega)$, respectively. The latter of these corresponds to the "reduced Raman spectrum"[16] and yields poor agreement with the position of the low-energy peak in the neutron results as well as in the relative weighting of low- and high-frequency bands.[17] In contrast, a simple linear variation of $\tilde{C}(\omega)$ yields a very good low-frequency-peak correspondence to the neutron data and a reasonable relative area of the high-frequency band. This conclusion is found to be relatively independent of the normalization factor for the bilayer background, although some shift of ~ ±5 cm^{-1} occurs for the low-frequency Raman peak of Fig. 2(a) for a range of plausible background estimates. Although such a simple linear form of $\tilde{C}(\omega)$ is not expected to hold in detail[18] for the entire spectral range, the results of Fig. 2 clearly demonstrate the importance of a frequency-dependent coupling parameter that tends to cancel the $\omega^{-1}(n+1)$ phonon displacement factor in $I_R(\omega)$.[1]

In summary, the observation of Raman scattering from amorphous transition-metal alloys utilizing IERS implies that the study of thin noncrystalline metals is now feasible. The peaks in the vibrational spectra provide information on the strength of interatomic interactions[13] as well as constraints for future structural models. Thin-film Raman studies will allow the study of the vibrational states of amorphous metal alloys over a broad range of compositions beyond the deep eutectic range of splat-cooled foils that may be readily studied by inelastic neutron scattering. Of particular interest are concentrated alloys with composition near that of pure a-Fe and a-Ni. Although the pure amorphous metals are unlikely to be stable, except perhaps at low temperatures, dilute alloys may be studied. The observation of Raman scattering using the trilayer method also implies that studies of structural relaxation are feasible for amorphous alloys. As such, the role of changes in structural order may be explored.

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[17] For isolated local B modes this area ratio approaches the composition rate of 2.

[18] Below ≈70±20 cm^{-1}, $g(\omega)$ and thus $\tilde{C}(\omega)$ are expected to vary as ω^2.