PHYSICAL REVIEW B VOLUME 39, NUMBER 9 15 MARCH 1989-II

Inelastic neutron scattering of amorphous $Ni_{0.95}Tb_{0.05}$

Raul Fainchtein* and Jeffrey S. Lannin
Department of Physics, Penn State Univeristy, University Park, Pennsylvania 16802
(Received 14 November 1988)

Inelastic–neutron-scattering measurements have been performed on low-temperature-deposited, thick magnetron-sputtered films of the dilute amorphous alloy a-$Ni_{0.95}Tb_{0.05}$. Averages over the modified dynamical structure factor, $G(Q,E)$, yield a phonon density of states with two features which approximately correspond to similar structure in fcc metals. The results thus indicate that quantitative disorder does not remove this form of the phonon spectrum. The spectra additionally suggest an ~17% reduction in first-neighbor Ni-Ni force constant relative to c-Ni due to changes in short-range order and packing density.

INTRODUCTION

Of basic importance in the field of noncrystalline solids is the extent to which structural disorder modifies the vibrational, electronic, and magnetic properties. Recent studies of elemental amorphous semiconductors have indicated the particular sensitivity of the vibrational states to changes in short-range order (SRO) between crystalline and amorphous systems.[1] In amorphous metals less is known about the influence of structural disorder on the vibrational states. Lattice-dynamical models of fcc metals and rare-gas solids exhibit a characteristic two-peaked structure for the acoustic band density of states, $G(E)$.[2] Theoretical studies also indicate that the effective force constants that dictate the form of the density of states for fcc transition metals fall rapidly with distance.[3] Various calculations performed on the corresponding amorphous transition or noble metals have differed in the extent to which the disordered state exhibits a broadened two-peaked $G(E)$ form paralleling that of fcc systems.[4–7] In particular, it has been suggested that structural disorder will eliminate the two peak character and result in an essentially structureless, single broad band. Implicit in these earlier studies was the belief, for example, that large fluctuations in first-neighbor distance would effectively yield a significant distribution of first-neighbor force constants. The resulting "quantitative" disorder was thus suggested to remove similarities between the phonon densities of states of crystalline and amorphous transition metals.[4,5] One exception to these studies was that of Yamamoto *et al.*, who specifically included quantitative disorder in their calculation for a-Fe.[7]

Up to this time no experimental determination of the density of states has been performed in amorphous metals that resolves the issue of the role of disorder on the vibrational spectrum for a pure amorphous metal. Prior amorphous metal alloy studies indicate either a single broad low-energy peak for metal-metal alloys[8] or a two-peak structure for metal-metalloid systems.[9,10] In both cases the low-energy spectra that correspond to acoustic states in fcc metals exhibits a single broad band. These studies have also been confined to more concentrated alloys and thus do not address models of pure elemental amorphous metals. As the latter are unstable at room temperature, it is necessary experimentally to approximate the pure systems by considering the dynamics of a dilute alloy.

Radial distribution function (RDF) studies of the dilute amorphous alloy a-$Ni_{0.95}Tb_{0.05}$ have indicated a static disorder of ~3% in the width of the lower half of the first peak.[11] The similar position of the first-neighbor peak to that of crystalline (c-) Ni and the moderate amorphous width indicate related SRO of ordered and disordered phases. The form of the RDF beyond its first peak and the slower radial rise of the integrated coordination number relative to that of fcc Ni also indicate differences in local order.

In the present study the first experimental determination of the approximate phonon density of states for a-$Ni_{0.95}Tb_{0.05}$ is presented that confirms the result of Yamamoto *et al.* Previous theoretical studies of amorphous metals have assumed first-neighbor constants equal to that of the crystalline counterparts. The results in a-$Ni_{0.95}Tb_{0.05}$ also indicate that the first-neighbor force constant for this alloy is reduced by ~17% from that of c-Ni. This decrease is attributed to changes in SRO, particularly the lower packing density in the amorphous state.

EXPERIMENT

Inelastic–neutron-scattering measurements were performed on the LRMECS spectrometer at the Intense Pulsed Neutron Source (IPNS) Facility at Argonne National Laboratory. For the incident energy of 60 meV, the average energy resolution was 5 meV. A large quantity, ~25 gm, of sample prepared by high-rate triode magnetron sputtering onto a liquid-nitrogen-cooled Al substrate was employed for inelastic–neutron-scattering studies. Portions of this sample were utilized for RDF measurements.[11] Differential scanning calorimetry indicated that this material is stable up to a crystallization temperature of ~250 °C. Neutron-scattering measurements were performed at 12 K to reduce multiphonon contributions. Detailed corrections for multiphonon and multiple scattering were estimated with modeling procedures discussed elsewhere.[9] The neutron weighted density of states was obtained by an average of the modified dynamical structure factor, $G(Q,E)$ over a Q range of neutron wave-vector transfers of 4.5–7.5 Å^{-1}. The modified structure factor $G(Q,E)$ is related to the dynamical structure factor $S(Q,E)$ by the relation

$$G(Q,E)=\frac{E}{n(E)+1}\frac{2\overline{m}}{\hbar^2Q^2}e^{2\overline{W}}S(Q,E) ,$$

where $\overline{m}$ is the mass of the unit scatterer; $n(E)+1$, the population factor; and $\overline{W}$, the average the Debye-Waller factor.[9] The neutron weighted density of states, $G(E)$, is equal to the sum of the weighted individual atom partial densities of states, $G_i(E)$, with weighting factors $\omega_i=c_i\sigma_i/m_i$, where c_i is the concentration, σ_i, the coherent cross section, and m_i the mass of the ith species.[10] For the present case the weighting factor for Tb is ~1% of Ni so that the neutron weighted density of states is a good first approximation to the true $G_{\rm Ni}(E)$ contribution.

RESULTS AND DISCUSSION

Examples of the $G(Q,E)$ spectra are shown in Fig. 1 for selected cuts in the three-dimensional $G(Q,E)$ surface for fixed values of either Q_i or E_i. These spectra exhibit general variations in spectral intensity for different Q values due to dynamical correlation effects. Prior Q-dependent amorphous metal studies have emphasized dispersional and pseudo-Brillouin zone boundary effects observable at lower Q and E values than those obtainable here.[8] The oscillatory behavior of Fig. 1(a) is qualitatively similar to that observed in theoretical studies of models of amorphous metals formed by numerical quenching of hard-sphere Lennard-Jones quenched glasses.[12] Differences exist, however, in the positions of local maxima and minima relative to that observed here. The oscillatory variation in Fig. 1(b) in the form of $G(Q_i,E)$ indicates that an appropriate average over Q is required to obtain $G(E)$. Figure 2 indicates the resulting Q averaged $G(E)$. The squares indicate individual data points whose noise may be estimated by the level of local fluctuations. The solid curve is a seven point smooth that illustrates the main features of $G(E)$. Below 6 meV the spectra have, for simplicity, been extrapolated to $E=0$ by a quadratic dependence on energy. The spectrum exhibits a major peak at 21 meV and a weaker peak or shoulder at ~32 meV. Evidence for the presence of the latter is distinctly indicated in a number of the individual $G(Q_i,E)$ spectra. The plateau in the observed $G(E)$ at ~29 meV also indicates evidence for two peak or peak and shoulder character of $G(E)$ given the present 5 meV resoltuion. A very weak feature at ~40 meV is also suggested. The intensity ratio of the 21- and 32-meV peaks in $G(E)$ is found to be an oscillatory function of Q with period of 3 Å^{-1} as shown in Fig. 3. In contrast to the elemental semiconductor a-Ge (Ref. 13) the oscillatory behavior for the ratio of the peak intensities is not periodic in first-

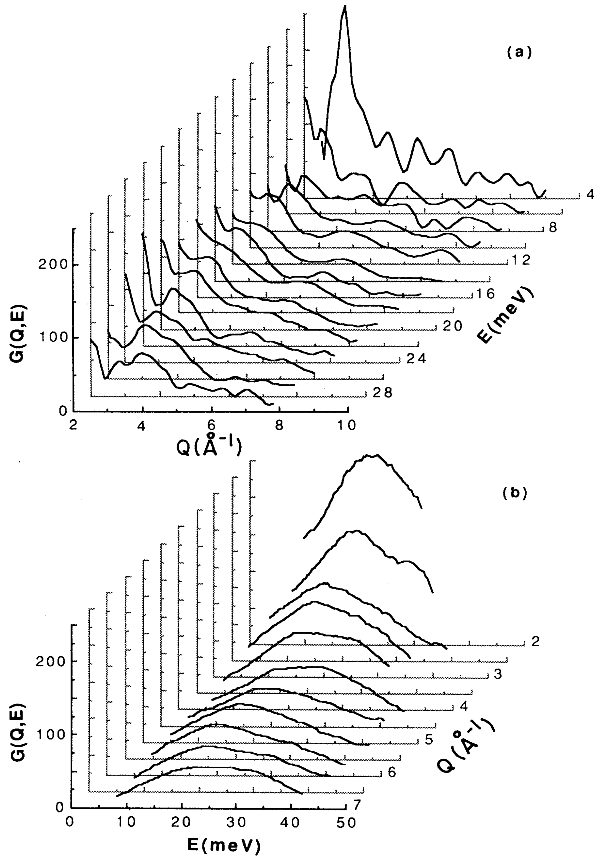

FIG. 1. Modified dynamical structure factor for a-$\rm Ni_{0.95}Tb_{0.05}$. (a) Cuts along the energy axis; (b) cuts along the momentum transfer axis.

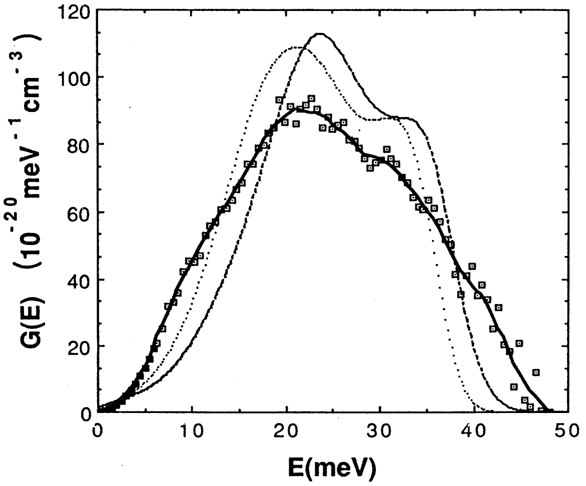

FIG. 2. Comparison of the experimental $G(E)$ of a-$\rm Ni_{0.95}Tb_{0.05}$ (open squares), and theoretical models for a-Ni (Ref. 6) (dashed line), and a-Fe (Ref. 7) (dotted). The theoretical spectra of have been broadened by the 5-meV experimental resolution. Solid squares at low E are a Debye extrapolation. The solid line is an additional seven point smoothing of the experimental data.

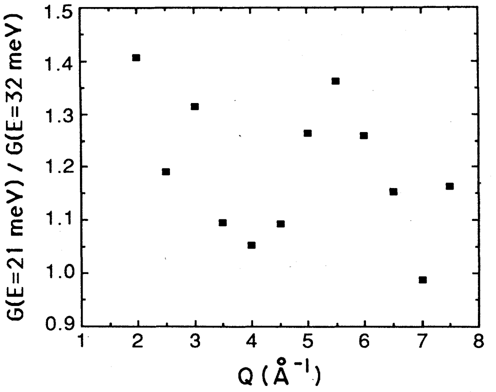

FIG. 3. Oscillatory behavior of the intensity ratio of the 21- to 32-meV features with Q of $G(Q,E)$.

neighbor distance. In the case of a-Ge this periodicity has been explained by a single-bond coherency mode.[14] Oscillatory $G(Q,E)$ variations in bulk a-$GeSe_2$ are also in accord with theoretical calculations of the vibrations of local tetrahedra.[15] For amorphous metals no predictions exist at this time for the peak–intensity-ratio variation that arises from dynamical correlations.

Figure 2 compares the area normalized experimental $G(E)$ with theoretical calculations for a-Ni of Thorpe *et al.*,[6] and a-Fe of Yamamoto *et al.*[7] The theoretical $G(E)$ spectra have been broadened by the 5-meV experimental resolution. Both calculations employed relaxed Bennett models[16,17] whose RDF's yield a very good correspondence to the RDF's and measured packing fraction. The model employed by Thorpe *et al.* yields excellent agreement with the RDF of the a-$Ni_{0.95}Tb_{0.05}$ in terms of the position and shape of the first peak. This implies, given predominant short-range interactions, that it is reasonable to compare the experimental, dilute alloy and theoretical pure a-Ni spectra. Both theoretical models in Fig. 2 exhibit qualitative agreement with experiment. The better peak position agreement for the Yamamoto *et al.* model may be fortuitous as it employed c-Fe force constants which are weaker than those of c-Ni. In the calculation of Thorpe *et al.*, all atoms with distances less than the minimum between the first and second RDF peaks interact with a single force constant, thus neglecting quantitative disorder. The use of this simple one parameter Born model yields good agreement with the estimated experimental density of states of c-Ni. If a similar force constant is employed for a-Ni the resulting spectral peaks occur, as Fig. 2 notes, at somewhat higher energies than experiment. If the theoretical spectrum of a-Ni is reduced by $\sim 8\%$ an improved agreement with experiment is obtained. This implies a force constant reduction of 17% relative to that of c-Ni. The reduction in first-neighbor interactions is attributed to differences in SRO and in packing density in the amorphous state.[11] The experimental results indicate, however, a considerably broader full width at half maximum associated with more extensive tailing than the broadened theoretical spectra.

The presence of 5% Tb in the present alloy is not expected to account for the apparent reduction in the Ni-Ni force constant relative to c-Ni. In particular, extended x-ray-absorption fine structure (EXAFS) studies in the related a-$Fe_{0.8}Tb_{0.2}$ system indicate a quite broad Fe-Tb peak at distances larger than the Fe-Fe peak.[18] This indicates both weak interactions between Tb and Fe and the absence of substantial Tb-Fe SRO. Significant correlations between Tb pairs were also found to not occur. These results, as well as optical and electron spectroscopy measurements[19,20] that exhibit small effects of Tb on the d-band states of c-Ni, indicate that the presence of Tb cannot account for the observed reduction in Ni-Ni force constant. The presence of Tb is expected, however, to result in increased disorder relative to that of a-Ni. As noted below, this may in part explain the broader nature of the alloy spectrum relative to theoretical calculations.

Although the broadened theoretical forms of $G(E)$ for a-Fe and a-Ni are rather similar, the Fe results of Yamamoto *et al.* yield slightly better agreement with experiment. This is attributed to the inclusion of quantitative disorder. The effect of this disorder on $G(E)$ within these models is not large. This is attributed to a narrower width of the first RDF peak relative to earlier estimates. The similarity between the experimental results and the theoretical models further suggests that the inclusion of force constant disorder does not remove the two peaked character of $G(E)$. While it is difficult to deconvolve our experimental spectrum to improve its resolution, the sharper unbroadened theoretical spectra suggest that a distinct two-peaked structure occurs in a-$Ni_{0.95}Tb_{0.05}$. In the unbroadened spectra, for example, of Thorpe *et al.*, the intensity ratio of the second peak to minimum at 29 meV is ~ 1.1. Higher-resolution studies would thus be useful to confirm this.

The theoretical results in Fig. 2, as well as other studies of amorphous metals, such as those of Rehr and Alben,[5] do not exhibit the high and low energy tails indicated in Fig. 2. It is possible that the differences between theory and experiment at low energy may be due to the influence of Tb. While the direct scattering from Tb atoms is small, interactions with Ni might result in additional low energy states. In Fig. 2 a weak shoulder at ~ 10 meV may have this origin. An additional source of low-energy states in $G(E)$ might occur due to atoms at larger first-neighbor distances, such as those in the highly asymmetric, second half tail of the first RDF peak.

The possible origin of the higher-energy tail states in the experimental $G(E)$ spectrum which is also noted in the individual $G(Q,E)$ of Fig. 1, is less clear. The narrow width of the first RDF peak of a-$Ni_{0.95}Tb_{0.05}$ implies a small number of atoms at short first-neighbor distances. While these might contribute to higher energy tail states, it is unclear that their number could account for the magnitude of $G(E)$. Similarly, the presence in the films of small quantities of argon whose cross section is quite low, could not account for the scattering. Additional calculations that include structural disorder, as well as possible effects of higher-neighbor disorder, would be useful. Thus, in contrast to amorphous semiconductors in which structural disorder results in an increase in lower energy, opticlike states,[1] the a-$Ni_{0.95}Tb_{0.05}$ differ in indicating additional possible high-energy tail related disorder.

In conclusion, the inelastic neutron spectra of a-$Ni_{0.95}Tb_{0.05}$ confirm the results of Yamamoto *et al.* and Thorpe *et al.,* indicating that two features are observed in $G(E)$ that correspond qualitatively to the two peaks in fcc transition metals. The results indicate that quantitative disorder effects in this system are not sufficiently large as to modify this conclusion. The similarity between the c-Ni $G(E)$ and that of the dilute amorphous alloy emphasize the importance of short-range order on the vibrational spectrum. Recent spectroscopic ellipsometry measurements of the dielectric spectra also indicate a relation between the broadened c-Ni and a-$Ni_{0.95}Tb_{0.05}$ electron states.[19] These similarities in physical properties and structure observed in RDF studies arise from the predominance of localized d-electron bonding. Thus, as in most elemental amorphous semiconductors, a correspondence between the phonon densities of states of amorphous and crystalline phases occurs when both short-range order and interactions are similar. Although the SRO of the amorphous and crystalline systems have considerable similarity, the observed reduction in nearest-neighbor force constant of the amorphous state, as well as changes in $G(E)$ imply that differences in local structural order are also important.

ACKNOWLEDGMENT

This work was supported by U.S. Department of Energy (DOE) Grant No. DE-GF01-84ER450995.

---

[*] Present address: Applied Physics Laboratory, Johns Hopkins University, Laurel, MD 20707-6099.

[1] J. S. Lannin, J. Non-Cryst. Solids **97/98**, 39 (1987).

[2] R. J. Birgeneau, J. Cordes, G. Dolling, and D. B. Woods, Phys. Rev. **136**, A1359 (1964).

[3] G. A. DeWit and B. N. Brockhouse, J. Appl. Phys. **39**, 451 (1968).

[4] A. Rahman, M. J. Mandell, and J. P. McTague, J. Chem. Phys. **64**, 1564 (1976).

[5] J. J. Rehr and R. Alben, Phys. Rev. B **16**, 2400 (1977).

[6] M. F. Thorpe, L. von Heimendahl, and R. Alben, in *Proceedings of the 3rd International Light Scattering Conference,* edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Wiley, New York, 1976), p. 668.

[7] R. Yamamoto, K. Haga, T. Mihara, and M. Doyama, J. Phys. F **10**, 1389 (1980).

[8] J. B. Suck and H. Rudin, in *Glassy Metals II,* edited by H. Beck and H. J. Güntherodt (Springer, Berlin, 1983), p. 217, and references therein.

[9] N. Lustig, J. S. Lannin, J. M. Carpenter, and R. Hasegawa, Phys. Rev. B **32**, 2778 (1985).

[10] N. Lustig, J. S. Lannin, and R. Hasegawa, Phys. Rev. B **34**, 6725 (1986).

[11] R. Fainchtein, J. S. Lannin, and D. L. Price, Phys. Rev. B **35**, 4258 (1987).

[12] G. Grest, S. Nagel, and A. Rahman, Phys. Rev. Lett. **49**, 1271 (1982).

[13] N. Maley, J. S. Lannin, and D. L. Price, Phys. Rev. Lett. **56**, 1720 (1986).

[14] D. Weaire and R. Alben, J. Phys. C **7**, 489 (1974).

[15] V. Walter, D. L. Price, S. Sussman, and K. J. Volin, Phys. Rev. B **37**, 4232 (1988).

[16] L. von Heimendahl, J. Phys. F **5**, 441 (1975).

[17] R. Yamamoto, K. Haga, H. Shibuta, and M. Doyama, J. Phys. F **8**, 479 (1978).

[18] M. G. Samant, C. J. Robinson, E. E. Marinero, and G. S. Cargill III, in *Proceedings of the Fourth International Conference on Structure of Non-Crystalline Materials, Oxnard, 1988* [J. Non-Cryst. Solids **106**, 178 (1988)].

[19] B. Y. Yang, P. Klosowsky, K. Vedam, and J. S. Lannin, in *Proceedings of the 6th International Conference on Rapidly Quenched Metals* [J. Mater. Sci. Eng. **99**, 281 (1988)]; Phys. Rev. B **38**, 1562 (1988).

[20] R. Levis and J. S. Lannin (unpublished).