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Vibrational density of states in amorphous $Ni_{1-x}B_x$ alloys and c-Ni_2B

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Inelastic neutron scattering measurements are reported on the amorphous (*a*) transition-metal—metalloid alloys of *a*-$Ni_{82}B_{18}$, *a*-$Ni_{67}B_{33}$, and the crystalline (*c*) compound, *c*-Ni_2B. The spectra provide information about changes in the vibrational density of states with composition and upon crystallization. The results of the crystalline-to-amorphous comparison for the 67 at. % Ni samples, show dramatic changes in the vibrational spectra, including an increase in the number of states, both at low and high energies, in the amorphous sample. The differences in the high-energy states are attributed to a change in short-range order between the amorphous and crystalline compositions. The similarities between the 67 at. % Ni and 82 at. %Ni samples are consistent with a similar short-range order in the two alloys, as well as comparable transition-metal—transition-metal and transition-metal—metalloid interactions. No evidence for any appreciable, direct metalloid-metalloid bonding in the high-metalloid-content samples has been found.

I. INTRODUCTION

Inelastic scattering experiments, such as neutron and light scattering, provide information on the vibrational dynamics and atomic-bond strengths, as well as place constraints on structural models of the amorphous state. Such information is needed in order to gain a fundamental understanding of the physical properties of amorphous solids. An important class of noncrystalline solids, that of amorphous (also know as glassy) metals are inherently difficult to study by optical means. The first light scattering experiments, performed on very thin film amorphous metals using interference-enhanced Raman spectroscopy, have only recently been reported.[1,2] The method of neutron scattering has been applied more extensively to amorphous metals especially since the large amounts of sample material which are required by such experiments have become available. Inelastic neutron measurements have been reported for a number of amorphous metal-metal (M-M) alloys[3] and for the transition-metal—metalloid $M^{(nd)}$-m alloys *a*-$Fe_{78}P_{22}$,[4] *a*-$Ni_{82}B_{18}$,[5] and *a*-$Pd_{80}Si_{20}$.[6]

In the present study we report the results of vibrational spectra measurements, using inelastic neutron scattering, for the $M^{(3d)}$-m alloys *a*-$Ni_{1-x}B_x$ ($x=0.18$ and 0.33) and the related polycrystalline compound, *c*-Ni_2B. The large mass ratio between the nickel and boron components ($m_{\mathrm{Ni}}/m_B=5.4$) allows for the observation of well-separated, acousticlike and opticlike bands in the vibrational spectrum. The *a*-$Ni_{1-x}B_x$ system is a unique $M^{(nd)}$-m alloy in that it can be quenched from the melt over a wider range of composition ($0.15 \lesssim x \lesssim 0.40$) than the typical *a*-$M^{(nd)}_{1-x}m_x$ alloy ($0.15 \lesssim x \lesssim 0.25$). This allows for a more extensive neutron study of the dynamics and the short-range order (SRO) in the Ni-B system as a function of the metalloid content than in the more conventional $M^{(nd)}$-m alloys. In a previous report we have compared the vibrational density of states and the $M^{(3d)}$-m bond strength in *a*-$Ni_{82}B_{18}$ and *a*-$Fe_{78}P_{22}$.[5] The SRO in the Ni-B system has been studied by a number of techniques over the past few years including neutron diffraction,[7–9] extended x-ray-absorption fine structure (EXAFS),[10] and NMR.[11] The conclusions of the present dynamical study of the Ni-B system will be compared to those obtained in the above measurements.

II. EXPERIMENT AND DATA REDUCTION

Time-of-flight inelastic neutron measurements were carried out at the Intense Pulse Neutron Source (IPNS) at Argonne National Laboratory, using the low-resolution medium-energy chopper spectrometer (LRMECS). Incident neutron energy of 112.6 meV was used and the scattered neutrons were detected by about 150 ^{3}He detectors, grouped into 47 units located between −7° and 116°. This allowed for the study of vibrational excitations up to ~ 90 meV, at momentum transfers as high as 9 $\mathrm{\AA}^{-1}$. The samples were splat-cooled glassy $Ni_{1-x}B_x$ ($x=0.18$ and 0.33) and powderlike polycrystalline *c*-Ni_2B. The sample temperature during the runs were kept at ~ 20 K to reduce multiphonon contributions to the scattering. The measured double differential cross sections were corrected for background scattering (empty can) and ^{3}He detector calibration. The calculated scattering law $S(\phi,E)$ at each detector angle ϕ was corrected for multiple scattering and multiphonon contribution. In addition, it was found necessary to subtract a small residual linear background from the spectra, the source of which is presently unknown. The vibrational density of states $G(E)$ was obtained from the generalized distribution function $G(Q,E)$ by averaging the latter over momentum transfers Q such that $5<Q<9$ $\mathrm{\AA}^{-1}$. It has been shown[4] that for multicomponent samples, $G(E)$ may be written as a weighted sum of partial densities of states, and is given by

$$G(E) \sim \sum_i w_i \langle (\hat{Q}\cdot \mathbf{e}_i)^2_E e^{-2W_i} \rangle g_i(E) ,$$

where $w_i = c_i \sigma_i / m_i$, σ_i is the bound-atom cross section, m_i is the atomic mass, c_i is the concentration, and $g_i(E)$ is the partial vibrational density of states of specie i. The factor in $\langle \ \rangle$ represents the average over Q of the neutron polarization factor and Debye-Waller contribution. A more detailed account of the data reduction procedure and theoretical background is presented in Ref. 4.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The measured $G(E)$ spectrum for a-$\mathrm{Ni}_{67}\mathrm{B}_{33}$ is shown in Fig. 1. It consists of two broad but distinct frequency bands. The low-frequency band centered about 21 meV is associated with motions involving Ni—Ni bonds, while the high-frequency band is associated with modes in which mostly the light B atoms are moving. There is substructure in both peaks. The low-frequency band has a shoulder at ~30 meV while the high-frequency peak is made up of two subpeaks at about 58 and 70 meV. The minimum or pseudogap in $G(E)$ occurs at 43 meV. Due to the finite resolution of the spectrometer, data below 9 meV was not accessible in this study, and was extrapolated to zero frequency assuming a quadratic Debye spectrum.

Crystalline $\mathrm{Ni}_2\mathrm{B}$ has the complex crystal structure of $\mathrm{Al}_2\mathrm{Cu}$ ($C16$), with 4 $\mathrm{Ni}_2\mathrm{B}$ units per unit cell.[12] The local environment around the B atom is that of an Archimedean antiprism (Fig. 5) in which each B atom is surrounded by 8 Ni atoms, and has two noninteracting B atoms at a distance of 2.12 Å. Each Ni atom is surrounded by a shell of four B atoms at 2.14 Å. In addition, there are 11 Ni atoms distributed in four different shells of 2.37, 2.43, 2.63 and 2.70 Å, from the central Ni atom, containing (1, 2, 4, and 4) atoms, respectively. The $G(E)$ spectrum for c-$\mathrm{Ni}_2\mathrm{B}$ is shown in Fig. 2. It has four sharp peaks at 21, 36, 48, and 60 meV. The two low-frequency peaks are separated by a pseudogap at 43 meV from the high-frequency optic modes. The low resolution (~9 meV) of this experiment means that the four peaks will be even sharper in the true density of states. In addition, the light-mass B atom is more "visible" than the Ni atom in a neutron experiment as $(\sigma/m)_{\mathrm{Ni}}(\sigma/m)_{\mathrm{B}} = 0.5$ This results in a more intense high-energy band than is expected in the true vibrational spectrum. The two low-frequency peaks in $G(E)$ for c-$\mathrm{Ni}_2\mathrm{B}$ fall close to the longitudinal and transverse acoustic phonon peaks in fcc Ni,[13] at 22 and 33 meV, though the intensity ratios are reversed. This reveral in intensities may be due to a contribution from low-energy optic modes in the c-$\mathrm{Ni}_2\mathrm{B}$ compound.

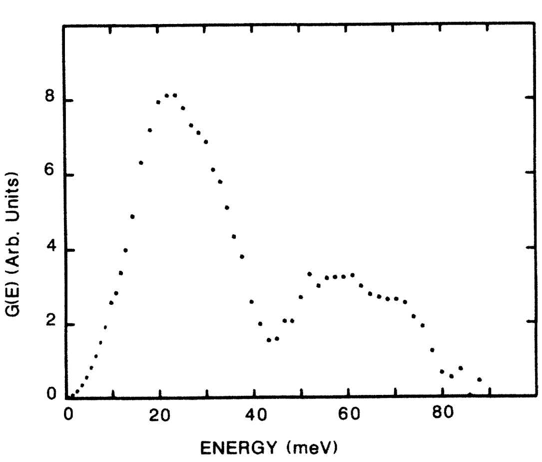

FIG. 1. Neutron-weighted vibrational density of states $G(E)$ for a-$\mathrm{Ni}_{67}\mathrm{B}_{33}$. The low-$E$ spectral range ($E \lesssim 9$ meV) has an assumed $G(E) \sim E^2$ behavior.

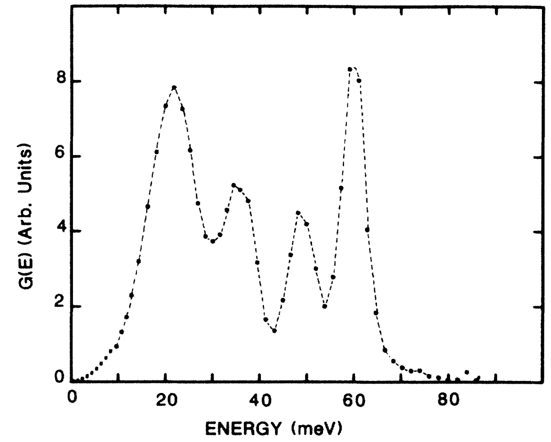

FIG. 2. Neutron-weighted vibrational density of states $G(E)$ for c-$\mathrm{Ni}_2\mathrm{B}$. The low-E spectral range ($E \lesssim 9$ meV) has an assumed $G(E) \sim E^2$ behavior.

Figure 3 compares the area-normalized c-$\mathrm{Ni}_2\mathrm{B}$ and the a-$\mathrm{Ni}_{67}\mathrm{B}_{33}$ $G(E)$ spectra. The most dramatic difference is the disappearance of the sharp peaks with disorder in both the high- and low-energy bands. In addition, there is an increase in the number of states in the amorphous system below 18 meV and above 65 meV, the latter being more noticeable. The pseudogap in the density of states remains at 43 meV for both systems. The disappearance of the sharp features in the spectrum of the amorphous system is associated with the absence of long-range order and is a "mark" of topologically disordered solids. The additional low-energy states, below ~18 meV, has been seen in other crystalline to amorphous comparisons[3,4] and appears to be a general result for the amorphous state. The origin of these low-energy states is not clear though various possible explanations have been suggested.[3] Their main influence is on the thermodynamic properties at low temperatures. For example, a Debye-type quadratic $G(E)$ assumed in Fig. 3 indicates larger differences in the phonon contribution to the specific heat at low temperatures. High resolution neutron scattering or Brillouin scattering would be useful in confirming this prediction. The additional states at low frequencies, along with the disappear-

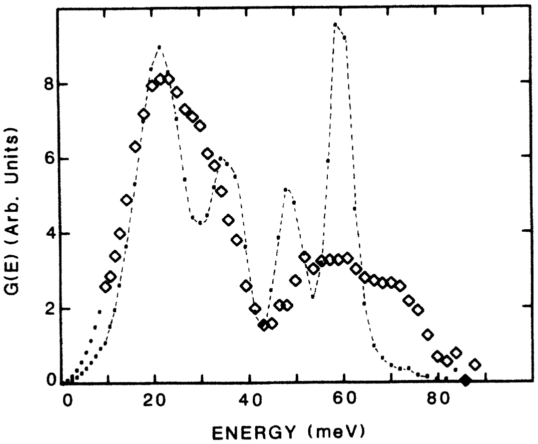

FIG. 3. Comparison of the area-normalized, neutron-weighted vibrational density of states $G(E)$ for a-$Ni_{67}B_{33}$ (◇) and c-Ni_2B (— — —).

ance of the sharp structure, may also be seen in a comparison of the scattering law $S(Q,E)$ for the two samples. Such a comparison is shown in Fig. 4 for a constant Q cut, at $Q=5.0$ Å^{-1}. The rising portion of the spectra below 10 meV is due to the resolution-broadened elastic peak.

At very high excitation energies, above 65 meV, the amorphous $G(E)$ spectrum reveals a substantially larger number of states than the crystalline spectrum. These "excess" states are more pronounced in this system than in any amorphous to crystalline comparison made to date. The origin of such high-energy states has been attributed to local high-density regions frozen in during the rapid quenching of the sample.[14] The presence of such "defects" should depend on preparation and on thermal treatment, and suggests the value of annealing studies to ascertain their existence. While the presence of such defects in the system may explain part of the additional intensity, comparable to that found in the a-$Fe_{78}P_{22}$ system,[4] it is not expected to account for the large number of excess states seen in the Ni-B system.

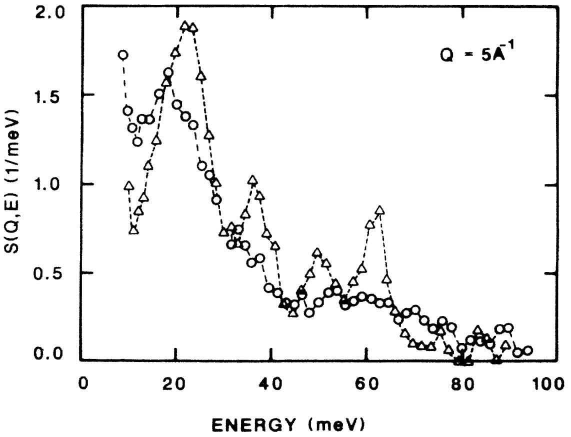

FIG. 4. Comparison between the scattering functions $S(Q,E)$ at $Q=5$ Å^{-1} for a-$Ni_{67}B_{33}$ (○) and c-Ni_2B(△).

Another possibility is the existence of a small number of B-B bonds, as was suggested by neutron-diffraction results.[7] Since the B atom is very light, modes involving interacting B atoms are expected to be characterized by frequencies as high as ~160 meV (1290 cm^{-1}), as determined by Raman scattering from a-B films.[15] The present results indicate a maximum vibrational energy of less than 90 meV. Measurements carried out in this work using higher incident neutron energies ($E_0=150$ meV), allowing for larger energy transfers to be probed, revealed no additional states beyond 90 meV. This does not rule out the existence of B-B bonds in the system, since their number may be too low to be detected. It is clear that as the boron content increases with alloying, there will be an onset of direct B-B bonding in the system.

A third possibility for the origin of the excess high-energy states is a rearrangement of the local near-neighbor configuration about the caged B atom in going from the crystalline to the amorphous composition. This change might lead to an increased interaction between the B and the Ni atoms around it, resulting in larger vibrational frequencies. The findings of the NMR experiments of Panisoid *et al.*[11] do indeed indicate a different atomic environment around the B atom upon crystallization. Also, Suzuki *et al.*[9] conclude from pulsed neutron diffraction results that the Ni atoms surrounding the B sites occupy the corners of distorted trigonal prisms, rather than Archimedean antiprisms (see Fig. 5). This last study also obtained a somewhat smaller B—Ni bond distance in the amorphous system than in the crystalline system. A smaller B—Ni bond length would result in a stronger metal-metalloid interaction, and be consistent with an increase in the number of states at high energy.

To further explore the question of the relationship between the SRO in the crystalline and amorphous structures, the phenomenologically broadened crystalline spectra $G^b(E)$ of c-Ni_2B is compared to the $G(E)$ for a-$Ni_{67}B_{33}$ in Fig. 6. The broadening has been achieved by convoluting the experimental $G(E)$ with a one-parameter Gaussian broadening function. From this comparison it is seen that the spectrum of a-$Ni_{67}B_{33}$ is not a broadened version of its crystalline counterpart for any frequency range. This result was found to be independent of the broadening parameters used for a number of plausible parameter values. Since the vibrational spectrum of an amorphous system is mainly determined by near-neighbor interactions,[16] and thus by its local atomic environment, it is concluded that the SRO in a-$Ni_{67}B_{33}$ is different from that in its crystalline analogue, c-Ni_2B. A similar conclusion was reached in the EXAFS study of Wong and Liebermann[10] for the Ni atom environment only. The present vibrational study is consistent with a rearrangement of the atomic environments both around the Ni and the B atoms.

In Fig. 7 the area normalized $G(E)$ for a-$Ni_{82}B_{18}$ and a-$Ni_{67}B_{33}$ are compared. The spectra are similar in shape and peak positions indicating that the short-range order does not change with the addition of B to the system. In particular, the fact that the maximum vibrational frequencies are at ~90 meV, is further evidence for the absence of B—B bonding in the 33% B sample. The main

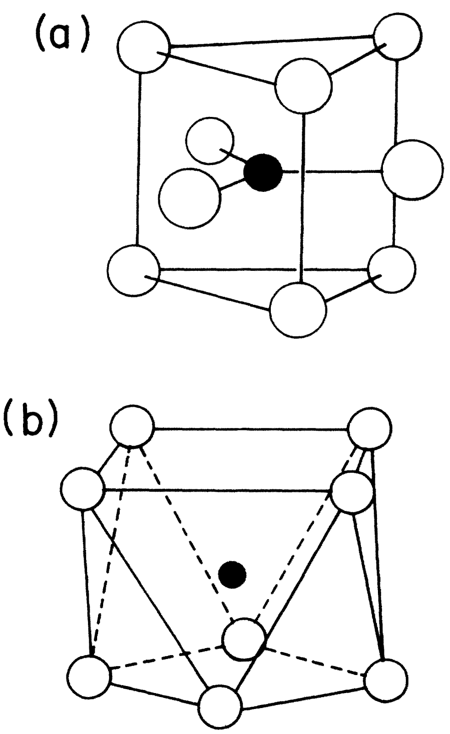

FIG. 5. (a) Trigonal prism configuration of transition metal atoms (open circles) about the metalloid atom (solid circles) in c-Ni$_3$B; (b) Archimedean antiprism configuration about the metalloid atom in c-Ni$_2$B.

difference between the $G(E)$ spectra is in the band-intensity ratios. There is a transfer of states from the high-energy band to the low-energy band as one goes from the 67 at. % Ni to the 82 at. % Ni sample. This is consistent with the low-energy peak corresponding mainly to Ni-Ni vibrations while the high-energy peak is governed by B-Ni vibrations. The 82 at. % Ni sample has substructure in the high-frequency band at 58 and 72 meV, similar to substructure seen in the 67% Ni sample. There is a shoulder in the low-energy band at ~32 meV as compared with the shoulder for the 67 at. % sample at ~30 meV. It is noted that this shoulder has shifted toward the longitudinal acoustic peak position of fcc Ni,[13] which is at ~33 meV, thus suggesting its origin is in the Ni-atom network. A similar observation was made in the a-Fe$_{78}$P$_{22}$ comparison with c-Fe.[4] The similarity in the Ni-Ni and B-Ni peak positions for the two compositions indicates comparable metal-metal and metalloid-metal bond strengths, as expected from their similar short-range orders.

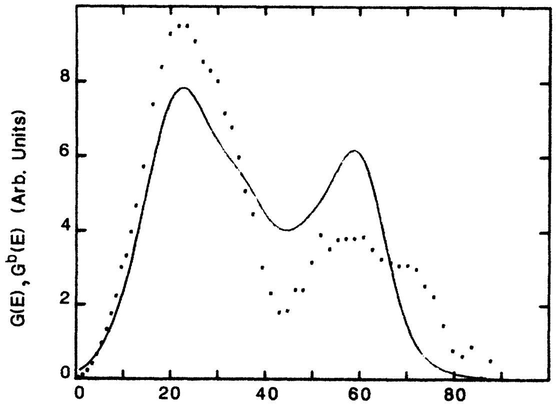

FIG. 6. Comparison of the area-normalized $G(E)$ spectra for a-Ni$_{67}$B$_{33}$ (dotted) with the phenomenologically broadened c-Ni$_2$B spectrum (solid), $G^b(E)$.

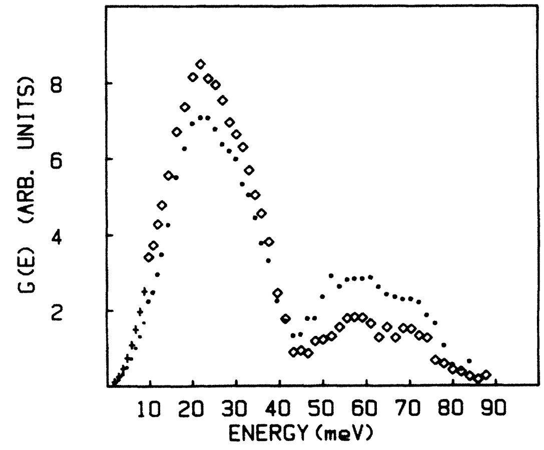

FIG. 7. Comparison of the area-normalized $G(E)$ spectra for a-Ni$_{67}$B$_{33}$ (dotted) with a-Ni$_{82}$B$_{18}$ (◇).

The ratios of the area of the low-frequency band (0–32 meV) to the high-frequency band (44–90 meV) are ~4 and ~2 for the 82 at. % and 67 at. % Ni alloys, respectively. The theoretical area ratios may be estimated from Eq. (1) by neglecting the polarization-dependent terms and assuming well-separated bands. Such an estimate gives area ratios of 2.48 and 1.10 for the 82 at. % and 67 at. % Ni alloys, respectively. As the polarization dependent terms in Eq. (1) are not expected to vary widely with energy,[4] this discrepancy indicates that there is considerable overlap between the bands. In particular, there is a proportionally more pronounced tailing of the B partial density of states (PDOS) to lower energies, below 43 meV, than that of the Ni PDOS above 43 meV. Similar results were obtained in the theoretical calculations of Ishii and Fujiwara for the Fe-P system.[17] This overlap prevents the extraction of the true vibrational density of states from the $G(E)$ spectrum, by simply multiplying, for example, the high-energy band by the ratio of the (σ/m) factors for the two bands.

IV. CONCLUSIONS

This inelastic neutron scattering study provides the neutron-weighted vibrational density of states $G(E)$ for a-Ni$_{67}$B$_{33}$, a-Ni$_{82}$B$_{18}$, and c-Ni$_2$B. The amorphous spectra consist of a two major frequency bands, acoustic and opticlike, associated with Ni-Ni and B-Ni vibrations, respectively. A comparison of the $G(E)$ spectra of a-Ni$_{67}$B$_{33}$ with its crystalline counterpart c-Ni$_2$B indicates additional states in the amorphous spectrum both at low and high energy, as well as the erosion of all the sharp features of the crystalline phase. The additional low-energy states, the magnitudes of which are comparable to other crystalline-to-amorphous comparisons, indicate a softening of the metal-metal bonds upon amorphization and predict different thermal properties for the amorphous system. The excess high-energy states are particularly numerous in this system and suggest a change in the local atomic structure around the B atoms. Further evidence for such a change is seen from the fact that the phenomenologically broadened c-Ni_2B spectrum does not correspond to the a-$Ni_{67}B_{33}$ spectrum, as well as from the similarity between the $G(E)$ spectra for a-$Ni_{82}B_{18}$ and a-$Ni_{67}B_{33}$. These results are consistent with a change from an Archimedean antiprism to a trigonal prismatic environment about the caged B atom, as was suggested by NMR (Ref. 11) and pulsed neutron studies[9] of the Ni-B system. No evidence for any appreciable, direct metalloid-metalloid bonding in the high-metalloid content alloy has been found.

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