Soft Transverse Phonons in Nonequilibrium fcc Al:Si Solid Solution Quenched under High Pressure

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We have determined for the first time the phonon density of states of a *nonequilibrium fcc* $Al_{0.94}Si_{0.06}$ *solid solution* quenched under high pressure by means of inelastic neutron scattering and low-temperature specific heat. When compared with aluminum, a large softening of the transverse acoustic modes is observed similar to that found in amorphous metals. This shows that a phonon softening can be found in *nonequilibrium crystalline alloys.* The nonequilibrium state is due to the metallic state of silicon atoms trapped in the fcc lattice during quenching.

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Recent experimental results on rapidly quenched Al:Si alloys[1] strongly suggest that the dynamical properties of these crystalline alloys are strongly affected by rapid quenching from the melt. Aluminum and silicon are usually immiscible elements and to obtain an increase of the silicon solubility requires techniques like melt spinning or splat cooling. By the use of either rapid solidification[1-3] or quenching under high pressure,[4,5] silicon atoms can be trapped in the fcc aluminum matrix, with concentrations up to 18% for the latter preparation method.[5] Moreover, these alloys have been shown to be in a nonequilibrium state as a large irreversible exothermal effect [an enthalpy variation up to 4.1 kJ/mol (Ref. 1)] has been measured during the segregation of the solid solution. As no structural transition occurs in the fcc aluminum matrix, this enthalpy difference has been attributed to the energy difference between the metallic state of silicon atoms in the fcc lattice and their covalent state in the segregated clusters with diamond symmetry. The metallic state of silicon in the fcc aluminum matrix is emphasized since the dissolution of a high concentration of silicon under high pressure requires a pressure of the same order of magnitude as the one used to reach the metallic state of bulk silicon[6] and since the atomic volume of the metallic silicon (15.5 $Å^3$ for β-Sn structure) is much closer to the aluminum atomic volume (16.6 $Å^3$) than that of the covalent silicon (20 $Å^3$). As indicated by a large increase of the superconducting transition temperature (up to 11 K for 18% of silicon in aluminum[5]) and by a steeper slope of the temperature dependence of the resistivity at low temperature in the quenched state,[1] the silicon atoms in the fcc lattice induce an enhancement of the electron-phonon coupling. This effect could be accompanied by a lattice instability due to the nonequilibrium state and associated with a characteristic change of the phonon density of states. From a general point of view, techniques used to put metallic alloys in nonequilibrium states, like rapid solidification from the melt, thin-film deposition, and irradiation,[7] have been shown to induce large changes in the dynamical properties of metallic alloys. In amorphous metallic alloys, this effect is seen in the large enhancement of the low-frequency phonon density of states as compared to crystalline alloys.[8-10] Recently, measurements of Young's modulus, neutron inelastic scattering, and low-temperature specific heat on the icosahedral alloys $Al_{86}Mn_{14}$,[11] $Pd_{58.8}Si_{20.6}U_{20.6}$,[12] and $Mg_3Zn_3Al_2$,[13] in a nonequilibrium state, have shown a similar phonon softening compared to the crystalline state. Hence the measurement of the phonon density of states of a quenched crystalline metal should be of importance to find out experimentally if the disorder in atomic positions as found in amorphous metals is a necessary condition for an enhancement of the low-frequency density of states of transverse-acoustic modes. This could also give some new insight into *the specific importance of the nonequilibrium state on the dynamical properties* of rapidly quenched metallic alloys as all the aforementioned systems, whether amorphous, quasicrystalline, or crystalline, are far from their crystalline equilibrium state (they generally exhibit a large irreversible exothermal effect, i.e., an enthalpy variation of several kilojoules per mole, at the transition between the quenched and equilibrium states[1,11,14,15]).

The high-pressure thermal quenching technique has been used since it is experimentally very effective in preventing silicon precipitation during quenching[4,5] (with use of the rapid solidification techniques,[1-3] it is very difficult to prepare Al:Si solid solution without a large amount of silicon clusters embedded). However, for silicon supersaturations higher than about 10 at.%, the solid solution is highly unstable at room temperature.[5] Therefore we have restricted ourselves to a silicon concentration of 6% as this enables us to prepare homogeneous samples quenched down to room temperature under a pressure of 40 kbar. Following the phase diagram under high pressures,[4] samples were prepared by our heating to 1000 K under 40 kbar for 1 h followed by quenching down to room temperature in about 10 s.[16] The quenching rate under pressure is provided by the thermal contact of the sample with the belt system: The samples were quenched by our turning off the power of the small inserted graphite heater. After quenching, the pressure was released and the sample was kept at about 273 K under atmospheric pressure. The samples were small cylinders roughly 9 mm in diameter and 6 mm in height. They were characterized by means of standard x-ray powder diffraction and by neutron powder diffraction of the instruments D1B and D1A at Institut Laue Langevin (Fig. 1). The main difference lies in the silicon peaks which have disappeared in the quenched state because of the dissolution of the silicon atoms into the aluminum matrix compared to the annealed state. The same effect was seen in all x-ray measurements. The full peak width at half maximum intensity of the fcc Al:Si peaks ($\Delta Q \simeq 0.01$ Å^{-1}) is mainly determined by the resolution curve of the neutron diffractometer: This shows that our samples are well crystallized with no important disorder in atomic positions which could explain the effects found in dynamical properties. A very large decrease of the fcc lattice parameter was observed in the quenched state ($a_{\mathrm{fcc}} \simeq 4.035$ Å) as compared to aluminum ($a_{\mathrm{Al}} = 4.049$ Å). Following the results of Ref. 2, this decrease of a_{fcc} would correspond to a complete dissolution of the silicon into the aluminum matrix. Thus our samples appear as homogeneous fcc $\mathrm{Al}_{0.94}\mathrm{Si}_{0.06}$ solid solutions with no detectable silicon clusters. The final set of samples used for the neutron-inelastic-scattering experiment was made of 44 cylinders, all prepared under identical experimental conditions. The aluminum reference sample had the same geometry and the same mass in order to have the best possible comparison.

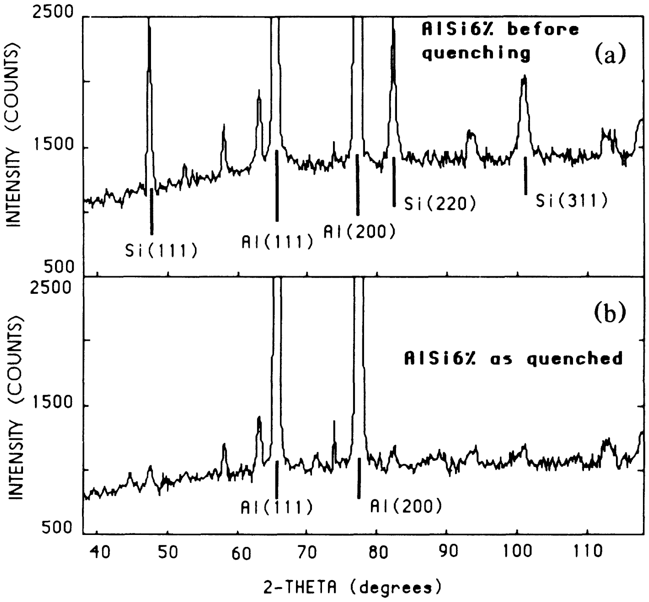

FIG. 1. Powder diffraction pattern of an $\mathrm{Al}_{0.94}\mathrm{Si}_{0.06}$ sample ($\lambda = 2.5$ Å, peaks without index are due to the sample holder). (a) Before quenching and (b) after quenching under high pressure.

The experiment was performed at the high-flux reactor of the Institut Laue Langevin on the thermal-neutron time-of-flight spectrometer IN4 with an incident energy of $E_0 = 68$ meV (resolution of $\Delta E/E = 4\%$) with use of scattering angles between 5° and 100°. Thus a complete sampling of the phonons of these coherent scatterers was guaranteed. Exactly the same corrections[8] have been used for both the $\mathrm{Al}_{0.94}\mathrm{Si}_{0.06}$ sample and the aluminum reference. In this binary alloy with two different neutron scatters, the *generalized* phonon density of states[8] (GPDOS) was determined from the weighted sum of the time-of-flight spectra. The inelastic spectrum obtained in neutron energy loss could only be separated from the region of the elastic peak at 12 meV. The remaining low-energy part of the phonon density of states was then completed with use of a Debye approximation [$G(\hbar\omega) \propto (\hbar\omega)^2$].[17] The GPDOS is normalized to 1 at 40 meV, the high-energy cutoff fixed for both samples. Both samples were measured at $T = 6$ K and 220 K. As the results do not show any significant difference [see the

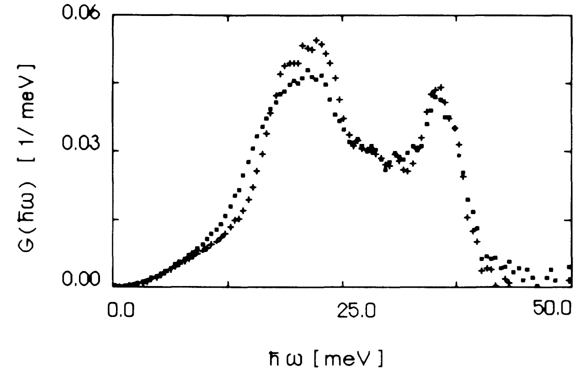

FIG. 2. Generalized phonon density of states for $\mathrm{Al}_{0.94}\mathrm{Si}_{0.06}$ samples (squares) and for pure aluminum samples (crosses) at $T = 6$ K.

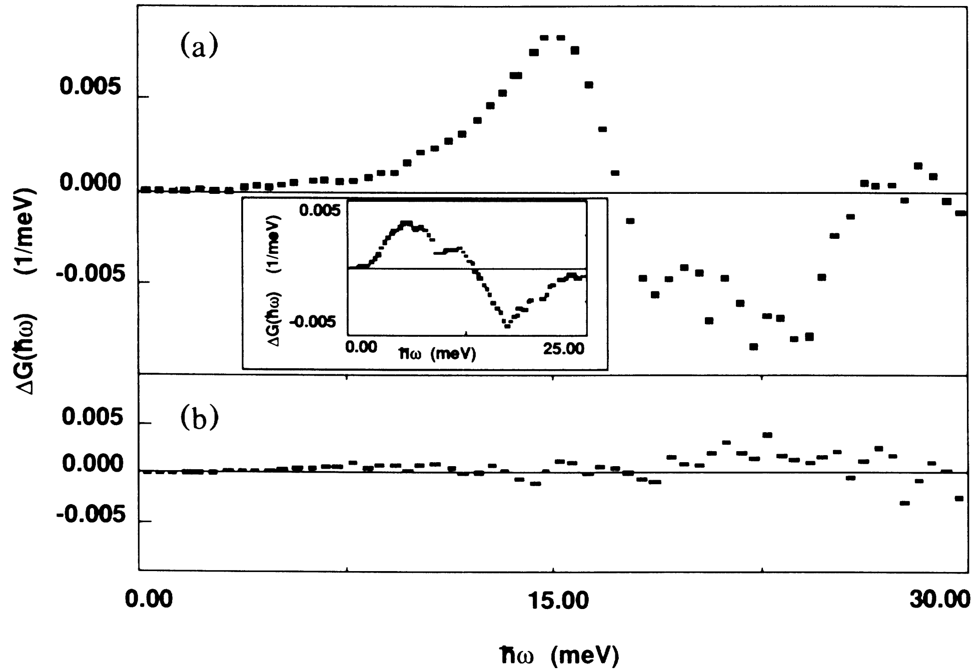

FIG. 3. (a) Difference between the GPDOS of $Al_{0.94}Si_{0.06}$ and of pure aluminum as seen in Fig. 2. Inset: Difference between the GPDOS of $Mg_{0.7}Zn_{0.3}$ in amorphous and crystalline states (from Ref. 19). (b) Difference between the GPDOS of $Al_{0.94}Si_{0.06}$ at $T=6$ and 220 K.

difference $\Delta G(\hbar\omega)=G_{6\mathrm{K}}(\hbar\omega)-G_{220\mathrm{K}}(\hbar\omega)$ for $Al_{0.94}Si_{0.06}$ in Fig. 3(b)] except a small hardening of the spectrum at $T=6$ K compared to $T=220$ K, only the result at $T=6$ K will be considered. The GPDOS of $Al_{0.94}Si_{0.06}$ and aluminum are compared in Fig. 2. The typical aluminum density of states is found, with the transverse-mode peaks around 20 meV and the contribution from the longitudinal mode at 35 meV as expected. For $Al_{0.94}Si_{0.06}$, the same general shape is preserved, as the sample is an aluminum-based fcc structure. For energies above 25 meV, we find no significant difference between $Al_{0.94}Si_{0.06}$ and Al.[18] The main difference lies in the energy region of the transverse-acoustic modes below 25 meV. Between 18 and 25 meV, the GPDOS is decreased in $Al_{0.94}Si_{0.06}$ as compared to Al, and below 18 meV it is largely increased. The magnitude of this effect can be seen in Fig. 3 where only the difference of the GPDOS $[\Delta G(\hbar\omega)=G_{Al_{0.94}Si_{0.06}}(\hbar\omega)-G_{Al}(\hbar\omega)]$ is plotted up to 30 meV. The striking similarity with amorphous alloys, e.g., $Mg_{0.7}Zn_{0.3}$,[19] as displayed in the inset, shows that fcc metastable Al:Si solid solution exhibits the same qualitative enhancement of the phonon density of states at low energy as a typical amorphous system, when compared to their respective crystalline reference. By our comparing the absolute scales in this difference of normalized GPDOS, it can be seen that the magnitude is even larger than that observed in this amorphous system and quite similar to the result for the quasicrystalline state of $Pd_{58.8}Si_{20.6}U_{20.6}$.[12] From the energy range where the softening is observed we conclude that the main contribution of the additional intensity is due to *a softening of the transverse phonons* in fcc $Al_{0.94}Si_{0.06}$ solid solution.

Figure 4 shows the specific heat at low temperature of an $Al_{0.94}Si_{0.06}$ alloy prepared under 60 kbar at 1000 K together with that of an annealed $Al_{0.94}Si_{0.06}$ alloy. The two main differences in the specific heat of these two samples are the higher lattice contribution to the specific heat in the quenched state and the jump of the specific heat at 2.5 K, the superconducting transition temperature, in the quenched state which is not seen in the an-

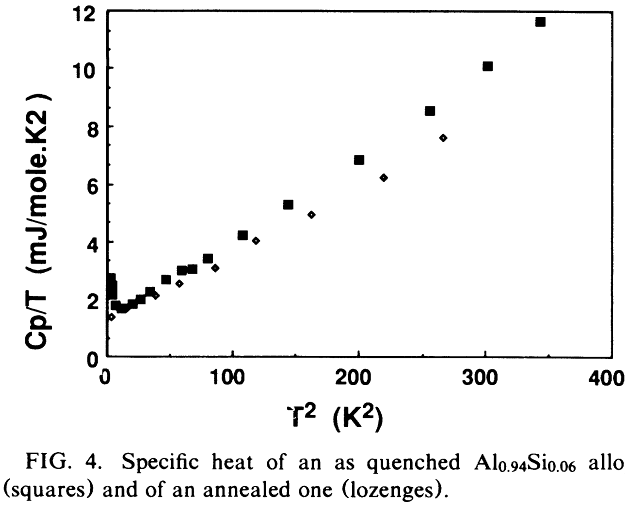

FIG. 4. Specific heat of an as quenched $Al_{0.94}Si_{0.06}$ alloy (squares) and of an annealed one (lozenges).

nealed state. We ascribe the enhanced βT^3 contribution to the specific heat to be caused by this softening of the phonon spectrum in the lowest part of the phonon spectrum, which we have observed by neutron spectroscopy at higher energy. The Debye temperatures determined from this measurement with no correction for the silicon phase, even in the annealed (segregated) state, gave $\Theta_D = 440$ K for the annealed state and $\Theta_D = 395$ K for the quenched state ($\Theta_D = 428$ K for pure fcc aluminum).[20]

In conclusion, we have shown that a large softening of transverse phonon modes exists in the nonequilibrium fcc $Al_{0.94}Si_{0.06}$ solid solution as compared to fcc aluminum. This is experimental evidence that the metallic state of silicon atoms in a crystalline metallic matrix, obtained as a nonequilibrium state through a quenching technique, is at the origin of an important shear lattice instability. The nonequilibrium state, in this crystalline material, is due to the metallic state of silicon atoms with twelve neighbors in fcc symmetry, which is a highly unstable configuration as compared to the four-coordinated covalent equilibrium state.[1]

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[17] This *underestimates* the real enhancement of the GPDOS at $\hbar\omega < 12$ meV.

[18] This is especially noticeable since, taking into account the similar masses of silicon and aluminum, one could expect some hardening of the atomic dynamics due to the lattice parameter decrease, which is not seen. However, as measurements on AlGe solid solutions prepared with the same techniques have shown similar T_c enhancements as that found in AlSi solid solutions (Refs. 1, 3, and 5), but with *an increase of the lattice parameter* mainly due to the Ge atomic size (Ref. 5), this lattice-parameter variation does not appear to be directly correlated with the changes of dynamical properties.

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