Comparison of Amorphous and Quasicrystalline Films of Sputtered $Al_{0.72}Mn_{0.22}Si_{0.06}$

J. L. Robertson and S. C. Moss
Physics Department, University of Houston, Houston, Texas 77004

and

K. G. Kreider
Center for Chemical Engineering, National Bureau of Standards, Gaithersburg, Maryland 20899

(Received 28 December 1987)

X-ray data were collected on films of $Al_{0.72}Mn_{0.22}Si_{0.06}$ sputtered on NaCl at 45, 150, and 230 °C. The 45 °C films show a typical metallic-glass structure factor, $S(Q)$, while at 230 °C the structure is quasicrystalline plus Al. A combined particle-size and phason strain broadening was applied to the normalized and reduced $S(Q)$ for the 230 °C film to bring it essentially into coincidence with the amorphous (45 °C) $S(Q)$ leading us to conclude that the glass, or amorphous, phase represents a defect limit of the quasicrystal.

PACS numbers: 61.50.Em, 61.40.+b, 61.55.Hg

Conventional microcrystalline models have for some time been considered unsuccessful descriptions of the glassy state of simple metals and alloys.[1] The discovery of the icosahedral quasicrystal,[2] however, has revived interest in the structure of metallic glasses. As discussed by Widom[3] in his review of icosahedral phases, there is an intimate connection between the local order in glasses, icosahedral quasicrystals, and the crystalline Frank-Kasper phases.[4] The competition among them may be understood if we consider the ways in which frustration, induced by an attempt to close-pack tetrahedra, is relieved or realized. Frank[5] was the first to point out that liquids can naturally accommodate this frustration by forming icosahedral clusters that are clearly not little pieces of, say, an fcc crystal. Sachdev and Nelson[6] have more recently developed the statistical mechanics of icosahedral order in dense liquids just above the glass transition and have calculated a structure factor, $S(Q)$, which agrees rather well with the data on amorphous Fe.[7]

For U-Pd-Si alloys, Kofalt *et al.*[8] have shown with x-ray scattering a similarity in the pair correlation functions, $G(r)$, for a quenched glass and a quasicrystal. Mayer *et al.*[9] have also done an electron-diffraction study to determine the $G(r)$ for an amorphous alloy of $Al_{0.84}V_{0.16}$, produced by electron irradiation of the quasicrystalline phase of the same alloy. In this work they demonstrate the similarity in structure between the "amorphized" quasicrystal and a conventional metallic glass. Urban Moser, and Kronmüller[10] had previously obtained a very fine grain size for the quasicrystalline phase by annealing the amorphous phase produced by irradiation and had termed the microstructure "microquasicrystalline." Bendersky and Ridder,[11] however, produced increasingly fine droplets—and hence cooling rates—from atomized $Al_{0.86}Mn^{0.14}$ alloys whose apparently amorphous structures, formed smoothly in the limit of high cooling rate, were not considered to be truly amorphous, as in a metallic glass, but rather "microquasicrystalline." Urban *et al.*[12] have reviewed this situation—glass versus microquasicrystal—and suggest that (a) the term "microquasicrystalline" may profitably be used only for the quasicrystal whose fine grain size, due to copious nucleation, cannot easily grow, and that (b) the competing amorphous phase, produced by irradiation, is indistinguishable from a conventional metallic glass. This resolution, while compelling, requires clarification because of both the Bendersky-Ridder result[11] and the present results, in which we are able to generate an excellent fit to an amorphous diffraction pattern by an appropriate broadening of the quasicrystal pattern of the same alloy.

In our experiments, 5-7-μm films of $Al_{0.72}Mn_{0.22}Si_{0.06}$ were rf magnetron sputtered in a 0.3-Pa pressure of argon onto substrates of NaCl held at $\simeq 45$, 150, and 230 °C as previously described.[13] The sputtered films were carefully removed from the NaCl in small flakes which were stacked in a sandwich of five or six pieces and held in a thin frame with a small circular window for x-ray transmission measurements. The x-ray data were collected on beam line X-14 of the Oak Ridge National Laboratory at the National Synchrotron Light Source at Brookhaven. A sagitally focused beam of $\lambda = 0.7271$ Å was used, and overlapping transmission and reflection data were collected over the range $2\theta = 0°$ to $136°$, where the scattering wave vector, Q, is given by $Q = 4\pi \sin\theta/\lambda$. All data sets were independently normalized by our adjusting the intensity at large Q to oscillate smoothly about the independent scattering curve for this alloy (plus calculated Compton scattering). Figure 1 shows the results for the structure factor, $S(Q)$, at the three deposition temperatures,

$$S(Q) = [I_m(Q)/N] - \langle f^2(Q)\rangle]/\langle f(Q)\rangle^2,$$

where $I_m(Q)$ is the measured (corrected) intensity, and the dispersion corrections to the x-ray scattering factors,

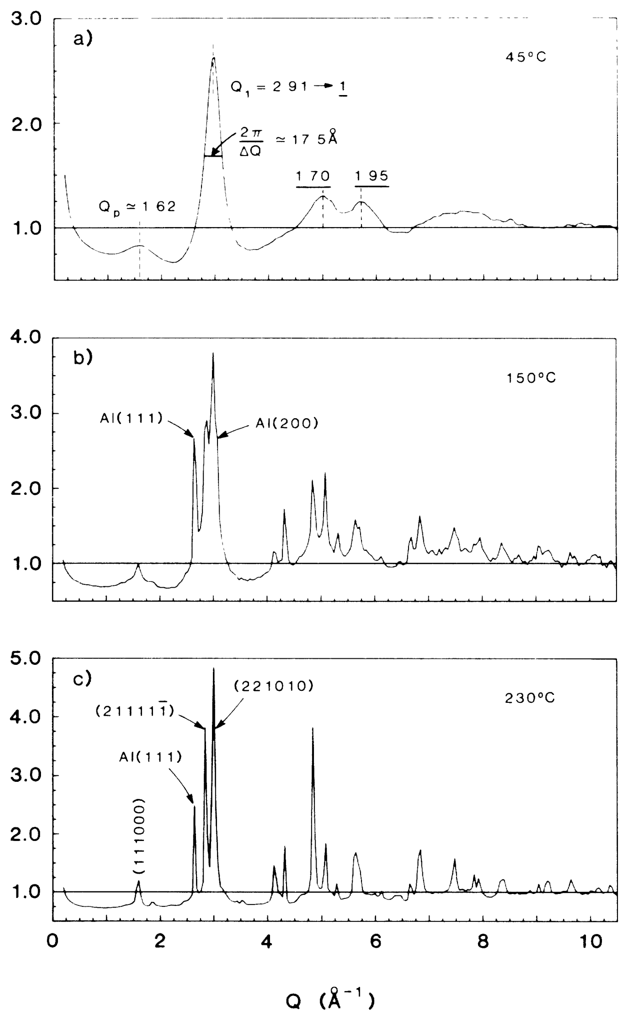

FIG. 1. $S(Q)$ for sputtered thin films of $Al_{0.72}Mn_{0.22}Si_{0.06}$ obtained from corrected and normalized synchrotron x-ray data. (a) A metallic-glass pattern for which typical features have been noted: Q_1, the first sharp diffraction peak; Q_p, the prepeak; and the correlation range, $2\pi/\Delta Q$. The major peak positions appear at the ratios 1:1.7:1.95. (b) $S(Q)$ for a film deposited at 150 °C in which the quasicrystalline and pure Al phases have begun to separate. (c) Fully developed quasicrystalline plus Al(111) pattern at 230 °C where all lines have been indexed (Ref. 14) and a few are noted for reference. (Note also the diminished small-angle scattering as Al and quasicrystal phase separate.)

$f(Q)$, were included in the averages.

$S(Q)$ for the sputtered amorphous phase is shown in Fig. 1(a) in which we have indicated several features that are common to metallic-glass patterns. There is a first sharp diffraction peak that is often associated with dominant intermolecular species in, for example, a dense random-packing model.[15] If we assume such a close packing of the principal metal-atom species, we can calculate roughly an atomic diameter as $d_1 \simeq 5\pi/2Q_1 \approx 2.70$ Å, which is smaller than the Goldschmidt diameter for Al of 2.86 Å. The peak width ΔQ yields roughly a correlation range of $\simeq 17.5$ Å, or about six interatomic diameters which is not uncommon for metallic glasses.[1] If we assign Q_1 a value of 1.0, the positions of the next two prominent peaks in $S(Q)$ scale to 1.7 and 1.95, much as observed in simple metallic glasses and close to the values of 1.7 and 2.0 suggested by Sachdev and Nelson.[16] The peak height at Q_1 in Fig. 1(a) is also quite reasonable for a metallic glass.[1]

Finally there is the diffuse prepeak[15] at $Q_p = 1.62$ Å^{-1}, associated with a distance of $d_p \simeq 5\pi/2Q_p \approx 4.85$ Å, which is interesting because it is an average of the Mn-Mn distances along an icosahedral edge in the shell of twelve Mn atoms of the distorted icosahedron in α-AlMnSi.[17] Figure 1(a) may then, over all, be interpreted as a conventional, chemically ordered, metallic-glass pattern with a minority-species prepeak. This agrees with the results of Dubois *et al.*,[18] who observed a very similar $S(Q)$ in their neutron study of liquid-quenched amorphous $Al_{0.70}Si_{0.17}Fe_{0.13}$.

Figure 1(b) shows $S(Q)$ for a film deposited at 150 °C in which the quasicrystalline peaks have appeared along with the (111) and (200) Al reflections. Were we to place Fig. 1(b) over Fig. 1(a), these quasicrystal peaks would seem to be developing out of the diffuse peaks. Figure 1(c) shows the fully developed quasicrystal pattern plus Al(111), where the (111) texture in the Al is more pronounced at 230 °C than at 150 °C. Icosahedral indexing can account for all of the assumed quasicrystal peaks, of which a few strong ones are labeled in Fig. 1(c) according to the scheme of Cahn *et al.*[14] The peaks in Fig. 1(c) are broader than those usually measured on melt-quenched samples,[19,20] indicating a smaller grain size for the sputtered film and a higher defect or phason strain[21,22] density. From a Gaussian fit to the Al(111) reflection, we estimate an Al particle size of $L \simeq 278$ Å. Because the Al and quasicrystal grains are intimately mixed, and both copiously nucleate but grow slowly, we assume that the quasicrystal particle size at 230 °C is also ≈ 280 Å; because of phason strain, a better estimate may not readily be made.

The rough correspondence of groups of quasicrystal peaks with the oscillations in the 45 °C data prompted us to attempt a calculation of $S(Q)$ in Fig. 1(a) by appropriate broadening of Fig. 1(c). Figure 2(a) shows the data in Fig. 1(c), with the Al(111) removed, convoluted with a normalized Lorentzian broadening function with a single width parameter chosen to fit the first sharp diffraction peak at $Q_1 = 2.91$ Å^{-1} in Fig. 1(a). The fit in Fig. 2(a) is remarkable in that it reproduces qualitatively all of the measured features; but it fails for the amplitudes and oscillations for $Q > 4$. The broadening function used for Fig. 2(a) may be associated with a particle size by our noting that the starting size is $\simeq 280$ Å. The size to which the convolution broadens can then straightforwardly be estimated to be $\simeq 25$ Å; i.e., the amorphous pattern in Fig. 1(a) may be tentatively

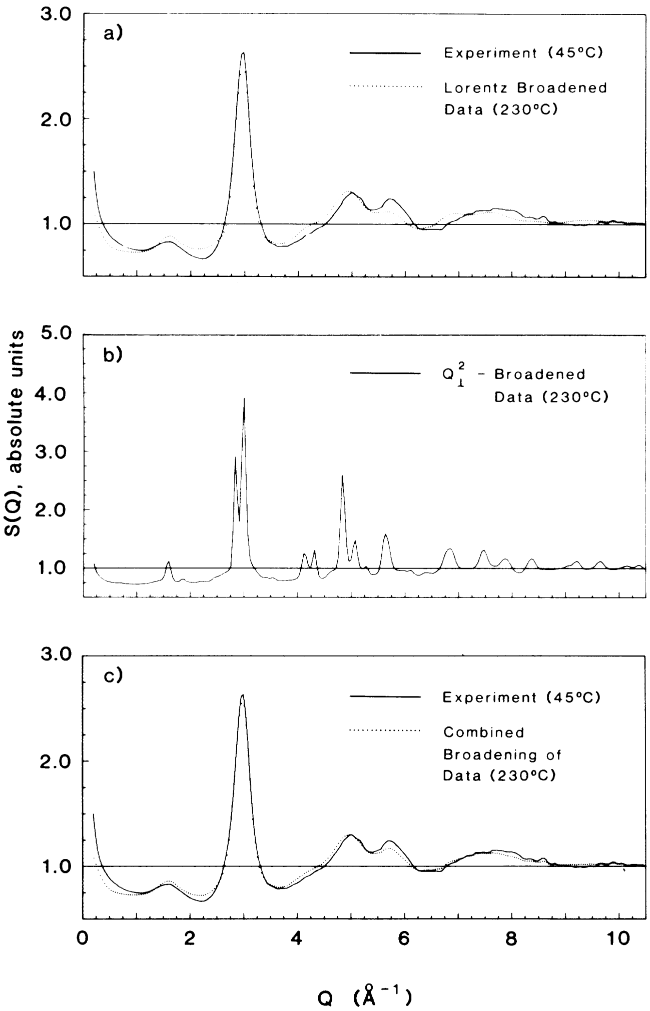

FIG. 2. (a) The best fit to Fig. 1(a) that could be accomplished by a Lorentzian broadening, associated with a particle size of $\simeq 25$ Å, of Fig. 1(c). (b) A pure phason-strain-broadened version of Fig. 1(c) in which each peak is broadened by an amount proportional to its $Q_\perp^2$ value (see text). (c) Our final best fit to Fig. 1(a) achieved through a combined particle-size and phason-strain broadening of Fig. 1(c) for which the particle size remains $\simeq 25$ Å.

attributed to a random quasicrystalline powder of $\simeq 25$ Å grain size. This interpretation is complicated by the fact that quasicrystal patterns, as in Fig. 1(c), are additionally broadened by phase defects or phason strain.[21,22] In melt-quenched samples, for example, 30-μm particles may show correlations ranges of only 300–500 Å.[19,20] Because this type of defect is inevitably associated with the growth of a quasicrystal, if we wish to treat Fig. 1(a) as a defective quasicrystal pattern we must introduce additional phason strain into Fig. 1(c).

Figure 2(b) shows the result of our introducing a Gaussian broadening of each peak in Fig. 1(c), with the Al(111) again removed, by an amount proportional to $Q_\perp^2$, i.e., proportional to the square of the perpendicular momentum transfer or its position relative to the acceptance function in the 6D representation of these crystal.[14,19–23] There are two aspects of this process requiring care. The first is in the treatment of the overlapping peaks with different values of $Q_\perp$. In these cases, we chose an effective broadening weighted according to the multiplicity of each, which, while not completely correct, does a reasonable job of assigning major weight. The second aspect is in the broadening of the individual peaks so as to include background correctly. This was done by our removing background, then broadening, and then restoring background smoothly. The broadening was made proportional to $Q_\perp^2$, rather than $Q_\perp$,[21,22] because of the assumed heavy density of defects. It does not much matter, however, because over the $Q_\perp$ range of our data, both will work well as a nonmonotonic source of Q-dependent broadening. The amount of the broadening in Fig. 2(b) is governed by a single parameter related to the density of phase defects. In our fit, this parameter is chosen so as to produce the best agreement with the measured curve in Fig. 1(a) in combination with a single-parameter Lorenztian broadening of nearly the same width as in Fig. 2(a) (the 25-Å estimate is unchanged). We consider the final two-parameter fit in Fig. 2(c) to be both excellent and provocative.

We have also compared our glass and quasicrystal patterns with powder patterns of α-AlMnSi kindly supplied by Yvonne Calvayrac. Strong peaks in the α and quasicrystal phases line up but we could find no simple way of converting the α-phase pattern into the glass although the similarity of local order in the quasicrystal and α phases has been demonstrated through detailed 3D and 6D Patterson analyses of neutron and x-ray powder patterns.[24] It therefore appears that while it is the intermediate-range order that distinguishes the phases, one cannot simply transform a crystal into a quasicrystal. What remains remarkable is that the sputtered-glass pattern, similar in most respects to a liquid-quenched metallic-glass pattern,[8,18] can be produced through a continuous transformation of the icosahedral quasicrystal. Our results therefore indicate that the atomic arrangements in the glass and quasicrystalline phases are quite similar, as posited by Sachdev and Nelson,[6,16] although in practice the transition between the two phases appears to occur by nucleation and growth and is characterized by a latent heat.[25,26] In recent differential scanning calorimetry on small pieces of our sputtered amorphous $Al_{4.75}Mn$ films,[27] a broad exotherm was observed well below crystallization indicating either a pronounced relaxation (and/or ordering) of the glass or a discontinuous transition to a demonstrably quasicrystalline phase. Preliminary x-ray examination of a sample heated to above this exotherm, however, shows only a sharpening of the amorphous pattern.[27] We are thus left with the following dilemma: Either our amorphous phase is not really amorphous but rather "microquasicrystalline," i.e., at the limiting case of fine grain size, or these ordered metallic glasses may be thought of as highly defective quasicrystals in which the orientational order is lost through the random orientation of local units. The transformation to a recognizable quasicrystal may then occur by very fine-scale nucleation of orientationally ordered material. We clearly prefer the second interpretation although, in a sense, our results may be used to support the first. Further structural studies are in progress to clarify this issue.

We acknowledge with thanks the assistance at the National Synchrotron Light Source of Dr. A. Habenschuss, of the Oak Ridge National Laboratory. We also thank Ms. L. C. Chen and Professor T. Spaepen for their differential-scanning calorimetry measurements on our films and for helpful suggestions, and Professor K. Urban for his correspondence. Work at Houston was supported by the National Science Foundation through Grant No. DMR-8603662.

---

[1] G. S. Cargill, III, in *Solid State Physics: Advances in Research and Applications,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1975), Vol. 30.

[2] D. Schechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[3] M. Widom, in "Aperiodic Crystals: Introduction to Quasicrystals," edited by M. V. Jaric (Academic, Boston, to be published).

[4] F. C. Frank and J. S. Kasper, Acta Crystallogr. **11**, 184 (1958), and **12**, 483 (1959).

[5] F. C. Frank, Proc. Roy. Soc. London A **215**, 43 (1952).

[6] S. Sachdev and D. R. Nelson, Phys. Rev. B **32**, 1480 (1985).

[7] J.-P. Lauriat, J. Non.-Cryst. Solids **55**, 77 (1983).

[8] D. D. Kofalt, S. Nanao, T. Egami, K. M. Wong, and S. J. Poon, Phys. Rev. Lett. **57**, 114 (1986).

[9] J. Mayer, K. Urban, J. Härle, and S. Steeb, Z. Naturforsch. **42a**, 113 (1987).

[10] K. Urban, N. Moser, and H. Kronmüller, Phys. Status Solidi (a) **91**, 411 (1985).

[11] L. A. Bendersky and S. D. Ridder, J. Mater. Res. **1**, 405 (1986).

[12] K. Urban, M. Bauer, A. Csanady, and J. Mayer, in Proceedings of the International Workshop on Quasicrystals, Beijing, 1987 (to be published).

[13] K. G. Kreider, F. S. Biancaniello, and M. J. Kaufman, Scr. Metall. **21**, 657 (1987).

[14] J. W. Cahn, D. Shechtman, and D. Gratias, J. Mater. Res. **1**, 13 (1986).

[15] S. C. Moss and D. L. Price, in *Physics of Disordered Materials,* edited by D. Adler, H. Fritzsche, and S. R. Ovshinsky (Plenum, New York, 1985).

[16] S. Sachdev and D. R. Nelson, Phys. Rev. B **32**, 4592 (1985).

[17] M. Cooper and K. Robinson, Acta Crystallogr. **20**, 614 (1966).

[18] J. M. Dubois, K. Dehghan, C. Janot, P. Chieux, and B. Chenal, J. Phys. (Paris), Colloq. (Suppl. 12) **46**, C8-461 (1985).

[19] P. A. Bancel, P. A. Heiney, P. W. Stephens, A. I. Goldman, and P. M. Horn, Phys. Rev. Lett. **54**, 2422 (1985).

[20] J. L. Robertson, M. E. Misenheimer, S. C. Moss, and L. A. Bendersky, Acta Metall. **34**, 2177 (1986).

[21] T. C. Lubensky, J. E. S. Socolar, P. J. Steinhardt, P. A. Bancel, and P. A. Heiney, Phys. Rev. Lett. **57**, 1440 (1986); P. M. Horn, W. Malzfeldt, D. P. DiVincenzo, J. Toner, and R. Gambino, Phys. Rev. Lett. **57**, 1444 (1986).

[22] J. E. S. Socolar and D. C. Wright, Phys. Rev. Lett. **59**, 221 (1987).

[23] V. Elser, in "Fractals, Quasicrystals, . . . ," edited by A. Amann, L. S. Cederbaum, and W. Gans, NATO Advanced Studies Institute Series (Kluwer Academic, Dordrecht, to be published).

[24] J. W. Cahn, D. Gratias, and B. Mozer, to be published; D. Gratias, J. W. Cahn, and B. Mozer, to be published.

[25] H. S. Chen and C. H. Chen, Phys. Rev. B **33**, 668 (1985).

[26] Y. Shen, S. J. Poon, and G. J. Shiflet, Phys. Rev. B **34**, 3516 (1986).

[27] L. C. Chen, F. Spaepen, J. L. Robertson, and S. C. Moss, unpublished.