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Structural relaxation in the $Al_{86}Mn_{14}$ quasicrystal

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Calorimetric and Young's-modulus measurements reveal that the as-spun $Al_{86}Mn_{14}$ quasicrystal exhibits structural relaxation at temperatures well below the icosahedral-orthorhombic transition. The enthalpy of relaxation is ≈ 90 cal/mol and the Young's modulus increases by $\approx 1\%$. The annealed samples upon heating show a reversible endothermic reaction of an elastic origin which is also reflected in the appearance of loss modulus. The activation energies of relaxation range from 42 to 51 kcal/mol. The relaxation behaviors of the $Al_{86}Mn_{14}$ quasicrystal are in many ways very similar to those of glassy $Al_{50}Si_{30}Mn_{20}$ and $Pd_{77}Cu_6Si_{17}$.

As-spun $Al_{86}Mn_{14}$ was found recently to have a long-range icosahedral orientation order with quasiperiodic rather than periodic translational order.[1] More recently, we[2] found in quenched $Al_{74}Si_6Mn_{20}$ alloy a quasicrystal "superlattice" which exhibits an electron diffraction pattern consistent with icosahedral point symmetry ($m\bar{3}5$). Various structural models have been proposed. Levine and Steinhardt[3] construct quasicrystals by extending the two-dimensional (2D) Penrose tiling concept. Phenomenological models based on Landau theory with quasiperiodic translational order and icosahedral point symmetry have also been proposed.[4–7] All the peaks observed in the electron and x-ray diffraction of quenched $Al_{86}Mn_{14}$ can be indexed with a quasilattice parameter using an icosahedral reciprocal lattice.[8,9]

There have been discussions concerning the generation of disorder in a three-dimensional Penrose tiling (3D PT) during a realistic growth process which would have matching-rule violations,[10] and the identification and stability defects, such as dislocations, in quasicrystals.[11] Furthermore, a review[12] by Nelson and Halperin suggests a possible structural relationship between quasicrystals and metallic glasses. Recent reports on the density,[13,14] Young's modulus, specific heat, and heat of transformation of icosahedral $Al_{86}Mn_{14}$ (Ref. 13) show that the changes in these physical properties are in many ways similar to those reported for metal glasses, and thus the icosahedral structure of $Al_{86}Mn_{14}$ is highly disordered and defective. In this Rapid Communication, we report evidence of structural relaxation in the icosahedral $Al_{86}Mn_{14}$ as observed by enthalpy and Young's-modulus measurements. It reveals, for the first time, regions of microscopic disorder in grown quasicrystals. For comparison, the kinetics of enthalpy relaxation of glassy $Al_{50}Si_{30}Mn_{20}$ are also presented.

$Al_{86}Mn_{14}$ and $Al_{50}Si_{30}Mn_{20}$ alloys were prepared by induction melting of high purity Al, Si, and Mn in a boron nitride crucible under argon atmosphere. Ribbon samples of about 1 mm in width and 30 μm in thickness were obtained by melt spun on a copper wheel ≈ 20 cm in diameter rotating at 2000 rpm in an argon atmosphere. Continuous long ribbons of ≥ 20 cm could be obtained for the $Al_{86}Mn_{14}$, but only short pieces (≤ 3 cm) could be obtained for the $Al_{50}Si_{30}Mn_{20}$. Samples were chemically thinned for TEM observations in an acid solution containing H_3PO_4, H_2SO_4, and HNO_3 at 75 °C. The temperature dependence of Young's-modulus sound velocity in $Al_{86}Mn_{14}$ was obtained by measuring the delay time (τ) of a 100-kHz Young's-modulus sound wave traveling in the sample. The accuracy of reduced delay time $\tau_r (= \tau/\tau_0)$ is better than 10^{-3}. The apparent specific heat C_p was measured with a Perkin-Elmer DSC-2 calorimeter. The accuracy of the data was approximately 0.2 cal/mol K for the absolute C_p values, but was better than 0.05 cal/mol K for the relative C_p values. Scanning rates are fixed at 40 K/min.

We found that the as-spun $Al_{86}Mn_{14}$ consists of domains of icosahedral phase in agreement with Shechtman, Bloch, Gratias, and Cahn,[1] while the as-spun $Al_{50}Si_{30}Mn_{20}$ is amorphous as evidenced from its diffuse diffraction rings [Fig. 1(b)]. As shown in Fig. 1(a), the $Al_{86}Mn_{14}$ is characterized by domains with elongated branches stemming from a central nodule within the domain and also by the fine speckles with sizes ≈ 150 Å in the domain. Selected area electron diffraction patterns show fivefold symmetry (see insert)

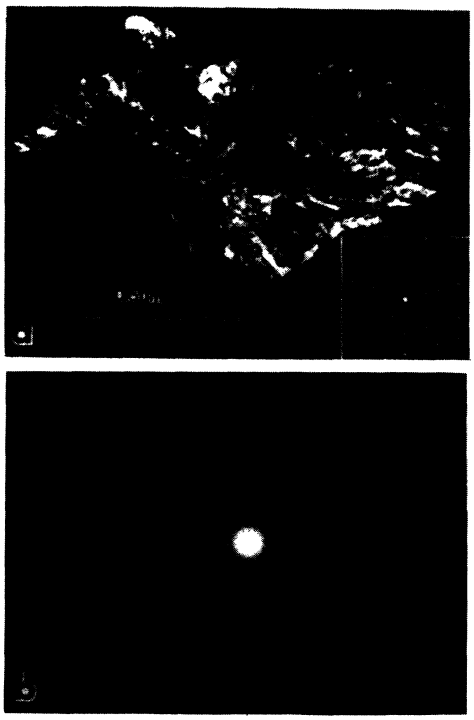

FIG. 1. TEM micrograph and diffraction pattern of (a) as-spun $Al_{86}Mn_{14}$ and (b) $Al_{50}Si_{30}Mn_{20}$.

consistent with an icosahedral point group $m\bar{3}\bar{5}$.

The rate of exothermic heat evolution (ΔC_p) and the integral heat evolution ΔH are shown in Fig. 2. We can see that the icosahedral $Al_{86}Mn_{14}$ transforms to the stable orthorhombic phase in the region 680–780 K, while the glassy $Al_{50}Si_{30}Mn_{20}$ crystallizes in two stages. The heat of transformation $\Delta H_t = 560$ cal/mol for the AlMn, and 920 and 670 cal/mol, respectively, for the first and second transformation in the AlSiMn. It should be noted that the main ΔC_p peaks are preceded by a gradual heat evolution beginning at ≈ 400 K (see also Fig. 3). Examination of the $Al_{86}Mn_{14}$ sample annealed at 600 K for 15 min in TEM reveals neither changes in domain structure (except for some slight contrast enhancement near the domain boundaries) nor any transformation of the icosahedral phase into the stable Al_6Mn.[13] We thus associate this with either some relaxation of the existing strains or structural relaxation into more ordered icosahedral structure somewhat similar to that observed in amorphous phase.[15] In the following, the kinetics of the relaxation is examined in details.

For the relaxation kinetics measurements, the as-quenched samples were subjected to annealing treatments at temperatures below the transition temperatures, $T_t \approx 680$ K, for various periods of time (1–65 h). The annealings were performed directly inside the calorimeter. Following the annealing treatment, the sample was thermally scanned at 40 K/min from 320 K to T_t to determine the specific heat ($C_{p,q}$) of the as-quenched samples and the $C_{p,a}$ of the annealed samples. It was then cooled (at the same rate, 40 K/min) to 320 K, and reheated immediately to obtain the $C_{p,a}$ data of the "reference" sample. This procedure is necessary to eliminate the uncertainty in the positioning of base lines. The change in the calorimetric behavior with annealing was used to monitor the structural relaxation processes.

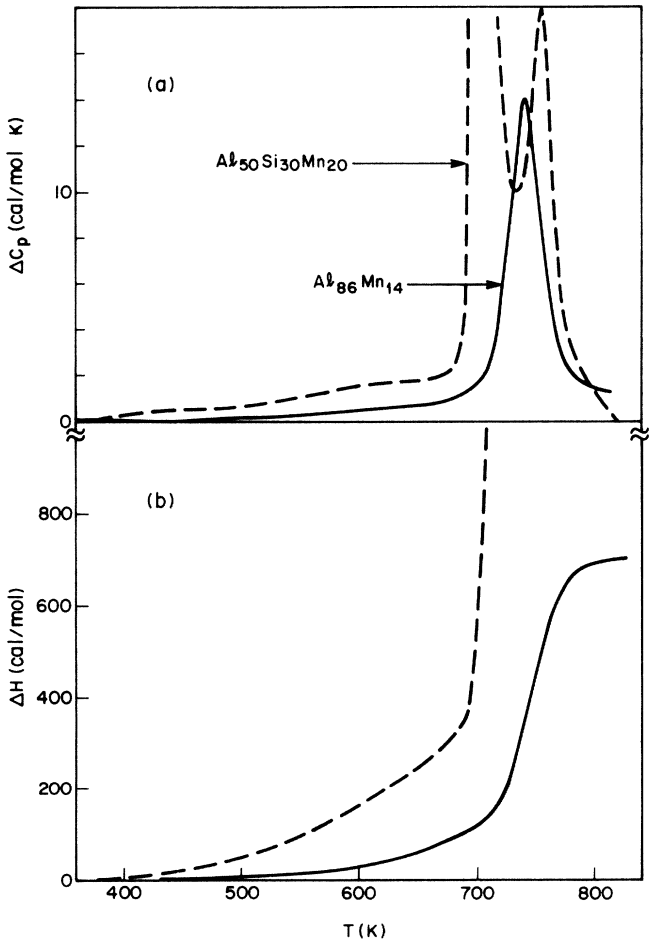

FIG. 2. (a) The rate of heat evolution ΔC_p and (b) the integral heat of transformation of the as-spun $Al_{86}Mn_{14}$ (——) and $Al_{50}Si_{30}Mn_{20}$ (– – –).

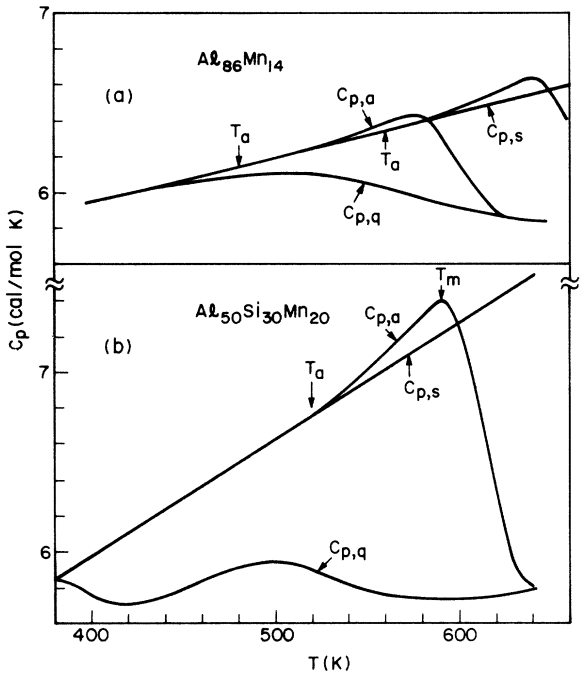

FIG. 3. Apparent specific heat C_p after various heat treatments.

Figure 3(a) shows the change in the thermograms of the icosahedral $Al_{86}Mn_{14}$ subjected to isochronal ($t_a = 16$ h) annealings at $T_a = 480$ and 560 K. As shown in Fig. 3(a), the C_p of the as-spun $Al_{86}Mn_{14}$($C_{p,q}$) falls on that of the reference sample C_{pa} near the room temperature, but deviates from $C_{p,a}$ at higher temperatures, indicative of a structural relaxation above 420 K. The heating curve of the annealed sample C_{pa} shows a $C_p(T)$ behavior which closely follows the $C_{p,a}(T)$ curve up to each T_a and then exhibits an excess endothermic peak before merging with $C_{p,q}(T)$ at higher temperatures. The excess endothermic peak is reversible while the exothermic process is irreversible and thus the annealing processes *couple* the reversible endothermic and irreversible exothermic reaction. These features are very similar to those observed for many metal glasses.[15] For comparison, corresponding thermograms of the glassy $Al_{50}Si_{30}Mn_{20}$ are shown in Fig. 3(b). It is noted that the glassy AlSiMn shows a higher temperature coefficient of $C_{p,a}$ (i.e., $dC_{p,a}/dT = 0.65 \times 10^{-2}$ cal/mol K^2) as compared to the icosahedral AlMn ($\approx 0.25 \times 10^{-2}$ cal/mol K^2).

The temperature of the endothermic peak T_m increases linearly with the logarithm of the annealing time ($\sim \ln t_a$) for both the AlMn and AlSiMn. We could calculate the activation energies $Q_m(T_m)$ for the structural relaxation from a series of $T_m(T_a, t_a)$ data that obeyed the following equa-

tion:[15]

$$Q_m(T_m)/k_B = d\ln t_a^*/d(1/T_a) \ , \quad (1)$$

where t_a^* is the annealing time for the appearance of ΔC_p peak at T_m and k_B is Boltzmann's constant. We found for both the icosahedral $Al_{86}Mn_{14}$ and the glassy $Al_{50}Si_{30}Mn_{20}$ that $Q_m(T_m)$ increases from 42 kcal/mol at 570 K to 51 kcal/mol at 610 K. These values are comparable to the activation energy of the icosahedral-orthorhombic transformation of the $Al_{86}Mn_{14}$, $Q_t = 53$ kcal/mol (Ref. 13) obtained previously using the generalized theory of phase transformation. Accordingly, we have also evaluated the activation energy of crystallization of glassy $Al_{50}Si_{30}Mn_{20}$, $Q_x = 78$ kcal/mol and an exponent $n = 2.5$.

The temperature dependence of the reduced delay time $\tau_r = \tau/\tau_o \simeq (E/E_0)^{-1/2}$ of $Al_{86}Mn_{14}$ samples is shown in Fig. 4, where E is the Young's modulus and the subscript o denotes as-quenched samples at room temperature. The measurements were taken during heating at a constant rate of 3 K/min. The samples were cycled in various temperature ranges to obtain data for different structural states. The as-spun sample (run 1) shows that τ_r increases linearly up to 400 K; above that a slight temperature dependence was observed. However the rate of the increase $d^2\tau_r/dT^2$ decreases (i.e., a deviation from the dashed line) above 430 K. This indicates the occurrence of some relaxation. The sample annealed at 640 K (run 2) shows that τ_r increases linearly, up to ≈ 570 K, with a slope $d\tau_r/dT = 2\times10^{-4}$ K^{-1} identical to that of the as-spun sample. At higher temperatures τ_r increases rapidly and peaks at the preannealed temperature ($=640$ K). τ_r then decreases due to the icosahedral-orthorhombic transformation. The third and fourth runs represent data, respectively, for the mixed phase of icosahedral and orthorhombic and for the stable orthorhombic phase. We note here that (1) the temperature coefficient of Young's modulus, $d\ln E/dT (\simeq -2d\tau_r/dT)$, shows a decrease above 300 K for the as-spun sample and at higher temperatures ≥ 570 K for the annealed sample (run 2). The loss in modulus may be attributed to an anelastic relaxation which has been observed commonly for metal glasses in the region of glass transition,[16,17] (2) the room temperature Young's modulus of the icosahedral phase increases by $\approx 1\%$ upon structural relaxation and increases drastically by $\approx 16\%$ upon a transition into the orthorhombic phase, and (3) the temperature coefficients $-d\ln E/dT$ of the intrinsic vibrational Young's modulus are higher for the icosahedral phase ($\approx 4.8\times10^{-4}$ K^{-1}) than for the orthorhombic phase ($\approx 2.8\times10^{-4}$ K^{-1}).

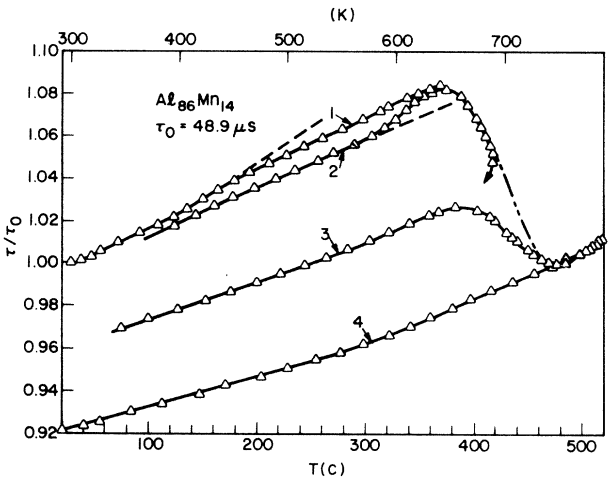

FIG. 4. The reduced delay time $\tau_r(=\tau/\tau_o)$ of the $Al_{86}Mn_{14}$ alloy.

Enthalpy and Young's-modulus measurements clearly demonstrate that the as-spun icosahedral $Al_{86}Mn_{14}$ relaxes at temperatures well below the icosahedral-orthorhombic transition. The heat of relaxation is ≈ 90 cal/mol which is about one-sixth of the heat of transformation ≈ 560 cal/mol. This is the same ratio observed for the glassy $Al_{50}Si_{20}Mn_{20}$ (Table I) and many metal glasses. It should be noted that the annealed samples show an excess endothermic specific heat [Fig. 3(a)]. This reversible enthalpy relaxation is anelastic in origin and arose from a relaxation mechanism similar to the two-level system.[17] The anelastic relaxation is also reflected in the pronounced loss in Young's modulus (Fig. 4). Annealing shifts the loss peak to higher temperatures. It is rather striking that relaxations in the icosahedral phase can occur with such short relaxation times, $\sim f^{-1} = 10^{-5}$ sec.

Present results are summarized in Table I and compared with data reported for $Pd_{77}Cu_6Si_{17}$ alloy glass.[13,16] We note that (1) the change in Young's modulus upon transformation ($\Delta E_t/E_o$) for the AlMn alloy is about two-thirds of that for the PdCuSi. This ratio is comparable to that for the heat of transformation between the two alloys. (2) The change in Young's modulus is large, $\approx 20\%$, which contrasts to only a slight change in density of $\approx 1\%$, and (3) the heat of structural relaxation is about one-fifth that of transformation (i.e., $\Delta H_\sigma/\Delta H_t \approx 0.20$) for both AlMn and AlSiMn. Based on the similarity in the changes in these physical

TABLE I. The density ρ (g/cm^3), Young's modulus E (10^{11} dyns/cm^2), the change in enthalpy ΔH (cal/mol) and activation energy Q (kcal/mol) of the icosahedral $Al_{86}Mn_{14}$ and glassy alloys $Al_{50}Si_{30}Mn_{14}$ and $Pd_{77}Cu_6Si_{17}$. The subscripts 0, σ, and t denote as-spun, structural relaxation, and transformation, respectively.

	ρ[a]	$\Delta\rho_t/\rho$[a]	E_0	$\Delta E_\sigma/E_\sigma$	$\Delta E_t/E_0$	$\Delta E_\sigma/E_t$	ΔH_σ	Q_σ	ΔH_t	Q_t	$\Delta H_\sigma/\Delta H_t$
$Al_{86}Mn_{14}$	3.26	1.0	10.12	0.01	0.16	0.06	90	42–51	560	53[a]	0.16
$Al_{50}Si_{30}Mn_{20}$	...	...	...	...	...	...	320	42–51	1600	78	0.20
$Pd_{77}Cu_6Si_{17}$	10.46	0.5	8.80	0.07	0.24	0.29	200	30	930	110	0.22

[a]Data of Ref. 10.

properties between the icosahedral $Al_{86}Mn_{14}$ and metal glasses, it has been inferred[13] that the icosahedral $Al_{86}Mn_{14}$ consists of a highly disordered defective structure. The observed structure-relaxation behaviors, the occurrence of relaxation well below the transition, the distribution in activation energies, the evolution of enthalpy and an increase in Young's modulus, and the appearance of the anelastic relaxation, as indicated by excess endothermic and loss modulus, would further substantiate the structural viewpoint.

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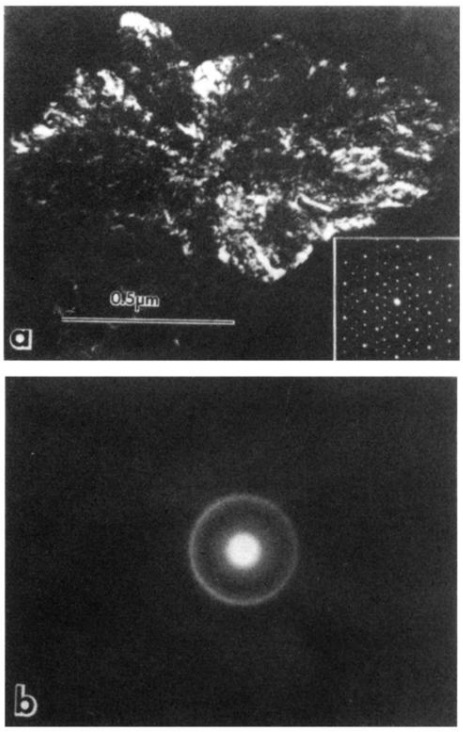
[1]D. Shechtman, I. Bloch, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1931 (1984).
[2]C. H. Chen and H. S. Chen (unpublished).
[3]D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).
[4]D. R. Nelson and S. Sachdev, Phys. Rev. B **32**, 4592 (1985).
[5]N. D. Mermin and S. M. Troian, Phys. Rev. Lett. **54**, 1524 (1985).
[6]D. Levine, T. C. Lubensky, S. Ostlund, S. Ramaswamy, P. J. Steinhardt, and J. Toner, Phys. Rev. Lett. **54**, 1520 (1985).
[7]Perk Bâk, Phys. Rev. Lett. **54**, 1517 (1985).
[8]Veit Elser, Phys. Rev. B **32**, 4892 (1985).
[9]P. A. Bancel, P. A. Heiney, P. W. Stephens, A. I. Goldman, and P. M. Horn, Phys. Rev. Lett. **54**, 2422 (1985).
[10]V. Elser, Phys. Rev. Lett. **54**, 1730 (1985).
[11]D. Levine *et al.*, Phys. Rev. Lett. **54**, 1520 (1985).
[12]D. R. Nelson and B. I. Halperin, Science **229**, 233 (1985).
[13]H. S. Chen, C. H. Chen, A. Inoue, and J. T. Krause, Phys. Rev. B **32**, 1940 (1985).
[14]K. F. Kelton and T. W. Wu, Appl. Phys. Lett. **46**, 1059 (1985).
[15]H. S. Chen, J. Appl. Phys. **52**, 1868 (1981).
[16]H. S. Chen, J. Appl. Phys. **49**, 3289 (1978).
[17]H. S. Chen and N. Morito, J. Non-Cryst. Solids **72**, 287 (1985).



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