$Al_{0.86}Mn_{0.14}$: a six-dimensional crystal

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The general properties of phases with the point symmetry group of an icosahedron and a long-range coordination order are analyzed. The probability for their formation during the rapid cooling of a liquid is discussed. A microscopic model for such a phase is also discussed.

Study of the alloy $Al_{0.86}Mn_{0.14}$ by low-energy electron diffraction (LEED) has shown that this material has the point symmetry of an icosahedron and a long-range coordination order (it has the capability of coherently scattering incident light).[1]

Let us examine some general properties of these structures. We assume that the homogeneous state is unstable with respect to the formation of a density wave with icosahedral symmetry:

$$\delta\rho(\mathbf{x}) = \rho_0 \sum_{i=1}^{6} \cos(k_0 \mathbf{n}_i \mathbf{x} + \alpha_i). \tag{1}$$

The $\mathbf{n}_i$ are unit vectors along the directions from the center to the corners of a regular icosahedron. Because of the nonlinear interaction of the density waves, harmonics

$\cos(k_0(N\cdot\mathbf{x})+\alpha)$ also appear, where $N=\Sigma_{i=1}^{6} z_i\mathbf{n}_i$ (the z_i are integers). It is easy to show that **N** does not vanish with any nonzero set of z_i; i.e., the vectors $\mathbf{n}_i$ are linearly independent on the field of rational numbers. For this reason, none of the phases α_i is fixed by nonlinear effects, and the energy of this system remains unchanged upon an arbitrary choice of the six quantities α_i. This means that there are six Goldstone modes, three of which are ordinary sound, while the rest are "phason" modes corresponding to displacements of harmonics of the density with respect to each other. Whether these modes are acoustic or diffusive depends on the specific structure of the system.

What is the most probable symmetry of the phase that forms upon the rapid cooling of the homogeneous system? Following Alexander and Mc Tague,[2] we expand the free energy of a slightly inhomogeneous system in powers of the density,

$$\Phi[\rho]=\Phi_2+\Phi_3+\ldots;\qquad \Phi_2=\sum_{\mathbf{q}}\mathbf{A}(|\mathbf{q}|)\rho_{\mathbf{q}}\rho_{-\mathbf{q}},$$
$$\Phi_3=\sum_{\mathbf{q}_1,\mathbf{q}_2}\mathbf{B}(\mathbf{q}_1,\mathbf{q}_2)\rho_{\mathbf{q}_1}\rho_{\mathbf{q}_2}\rho_{-\mathbf{q}_1-\mathbf{q}_2}, \tag{2}$$

and we determine $C=|\Phi_3|/\Phi_2^{3/2}$ for the density modulations corresponding to various symmetries. This quantity is a measure of the height of the "potential barrier" which the system must surmount upon the transition to the inhomogeneous state. For simplicity, we assume $A(|\mathbf{q}|)=A_0+A_1(|\mathbf{q}|/k_0-1)^2$ and $B(\mathbf{q}_1,\mathbf{q}_2)=B_0$. Furthermore, according to Ref. 2, we must assume that the density modulation should be chosen in the form $\delta\rho(\mathbf{x})=\rho_0\,\Sigma_i\times\cos(k_0(\mathbf{n}_i\cdot\mathbf{x})+\alpha_i)$, where the $\mathbf{n}_i$ are a set of unit vectors having the necessary symmetry group. It is assumed here that conditions do not favor the spontaneous appearance of higher harmonics, which are instead formed by nonlinear effects. If $A_0\simeq A_1$, this assumption is valid only if the wave vectors of the higher harmonics are substantially different from $k_0\mathbf{n}_i$. For the case of icosahedral symmetry, this condition breaks down even for the second harmonics (the edge of an icosahedron is only 5% longer than the distance from the center to a corner). Consequently, the conclusion reached in Ref. 2 that a bcc structure is more probable than an icosahedral structure ($C_{\text{bcc}}/C_{\text{icos}}=\sqrt{5/2}$) is unconvincing. When we simultaneously take into account the first and second harmonics by choosing a density modulation

$$\delta\rho(\mathbf{x})=\rho_0\Big(\lambda_1\sum_{i=1}^{6}\cos[k(\mathbf{n}_i\cdot\mathbf{x})]+\lambda_2\sum_{i,j=1}^{6}\cos(k[(\mathbf{n}_i-\mathbf{n}_j)\cdot\mathbf{x}])\Big) \tag{3}$$

(the second summation runs over the adjacent corners of the icosahedron), we find

$$C_{\text{bcc}}/C_{\text{icos}}>1\quad\text{for}\quad A_1/A_0>69. \tag{4}$$

The condition for the formation of the icosahedral phase is not a stringent one. Consequently, although this phase is metastable,[1] its formation upon rapid cooling may sometimes be more probable than the formation of other phases.

An interesting question is how such a phase can be constructed at the microscopic scale. Since the icosahedral group has a fivefold symmetry axis, this symmetry is incompatible with a crystal lattice, and the long-range coordination order in this phase

is less trivial than in ordinary crystals.

We can propose a model which shows how such an order can arise from the nearest icosahedral ordering of bonds, which is frequently encountered in metallic glasses.

We consider a six-dimensional real space R^6, in which there is a cubic lattice with a period of $2^{1/2}$. In R^6 we nest the space R^3, in such a manner that upon an orthogonal projection onto it the basis vectors of the lattice, $\{\pm \mathbf{e}_i\}_{i=1,\ldots,6}$, coincide with unit vectors running along the directions from the center to the corners of the regular icosahedron. Upon a projeciton onto R^{3*}—the orthogonal complement of R^3—the vectors $\pm \mathbf{e}_i$ then transform into $\pm \mathbf{m}_i$, whose tips also lie at the corners of a regular icosahedron. If we now single out from the lattice sites in R^6 those sites whose projections onto R^{3*} fall within an icosahedron with corners $\pm(3/2)\pm \mathbf{m}_i$, i.e., if we cut a "tube" out of R^6 and then project the contents of the tube onto R^3, then the distance between any two points of this projection will be no less than unity. The bonds between nearest neighbors will be ordered icosahedrically, although some of them will be ruptured. That the resulting distribution of points has a long-range coordination order can be seen from its Fourier transform, which is the convolution of the Fourier transform of the lattice in R^6 with the Fourier transform of the tube, limited to the R^3 momentum space:

$$\rho_{\mathbf{k}} = \int \rho(\mathbf{r}) e^{-i\mathbf{kr}} d^3\mathbf{r} = (2\pi)^{-3} \int [(\sum_N \delta(\mathbf{K}-\mathbf{K}_N)) * (\delta(\mathbf{k}) F(\mathbf{k}^*))] \delta(\mathbf{k}^*) d^3\mathbf{k}^*$$

$$= (2\pi)^{-3} \sum_N \delta(\mathbf{k}-\mathbf{k}_N) F(\mathbf{k}_N^*); \qquad F(\mathbf{k}^*) = \int e^{-i\mathbf{k}^*\mathbf{r}^*} \theta_T(\mathbf{r}^*) d^3\mathbf{r}^*, \tag{5}$$

where $\mathbf{r}$, $\mathbf{k}$, $\mathbf{r}^*$, and $\mathbf{k}^*$ are the components of $\mathbf{R}$ and $\mathbf{K}$ along R^3 and R^{3*}, respectively; K_N is a reciprocal-lattice vector in R^6; and $\theta_T(\mathbf{r}^*)$ is unity for points inside the tube and zero otherwise. We find a system of δ-functions, whose coefficients, which determine the brightness of LEED reflections, are given by the standard function $F(k_N^*)$. Working from the stoichiometry of the alloy $Al_{0.86}Mn_{0.14}$, we have assumed that each Mn atom is the center of an $Al_{12}Mn$ icosahedral cluster, while the Al atoms belong, on the average, to two identically oriented neighboring clusters. Correspondingly, in R^6 the Mn atoms lie at the sites of a simple cubic lattice, while the Al atoms lie at the centers of edges. The experiments of Ref. 1, however, show that the surface of this material may have an unusual structure. Specifically, the fact that the LEED pattern for a surface perpendicular to a twofold axis cannot be obtained through a projection of the same three-dimensional Fourier transform as in the cases of threefold and fivefold axes indicates that there may be a change in the lattice structure near this surface. We have adopted the opposite assumption, that the surfaces perpendicular to the threefold and fivefold axes do not change structure, and we have calculated the corresponding LEED pattern, using the model proposed above (Fig. 1). The agreement with the experimental data of Ref. 1 is encouraging.

We note in conclusion that the three phason modes acquire a clear meaning in this model: They correspond to displacements of the tube along R^{3*}. Since these displacements require finite jumps of atoms, the additional modes are diffusive.

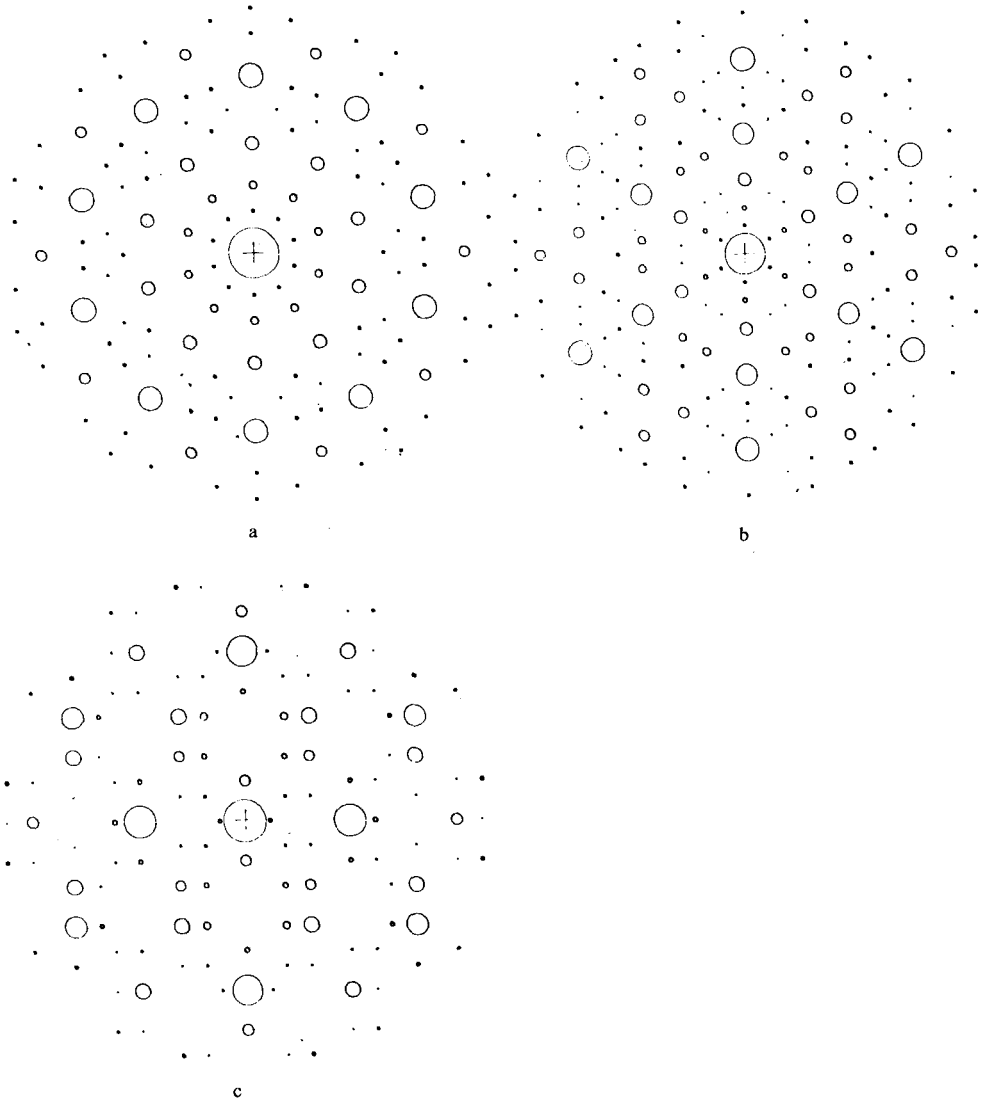

FIG. 1. Projections of the Fourier transform of the lattice onto planes perpendicular to fivefold (a), threefold (b), and twofold (c) axes. The size of a circle corresponds to the brightness of the corresponding peak. The form factor of the "tube" is chosen in the form $F(|\mathbf{k}^*|) = (|\mathbf{k}^*|R)^{-3} \times (\sin(|\mathbf{k}^*|R) - (|\mathbf{k}^*|R)\cos(|\mathbf{k}^*|R))$, where $R = 1, 2$. The projections of points lying in the region $|\mathbf{k}^*| < 13.3$, $|\mathbf{k}| < 4.2$, are shown.

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After this letter had been submitted for publication, we learned of a paper by Levine and Steinhardt,[3] who have developed an alternative approach. We are not able to compare that approach with our own, but we do note that the construction of Ref. 3 has a symmetry center and thus no phasons.

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[2]S. Alexander and J. Mc Tague, Phys. Rev. Lett. **41**, 702 (1978).
[3]D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).

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