Should All Crystals Be bcc? Landau Theory of Solidification and Crystal Nucleation

S. Alexander[a]
Department of Physics, University of California, Los Angeles, California 90024

and

J. McTague
Department of Chemistry and Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024

Very general symmetry considerations uniquely favor a bcc crystal structure near the melting line. This agrees with observations that almost all metals on the left-hand side of the periodic table are bcc at high temperature, and that, even where other structures are more stable, the first phase nucleated on rapid cooling can be bcc. Furthermore, icosahedral local symmetries are favored in amorphous solids. Fluctuation effects cause the transition from isotropic liquid to crystal to be first order in any dimension.

The structures of solids near the melting line are often different from those predicted by energy criteria. Furthermore, it is observed that crystal nucleation is selectively inhibited for some structures, leading to the formation of metastable crystals or glasses. For instance, the high-temperature crystal structures of all the metallic elements on the left-hand side of the periodic table (groups IA, IIA, IIIB–VIB) with the exception of Mg, together with almost all the lanthanides and actinides are known to be bcc near the melting line at low pressure. Most, however, transform to other structures at low temperature. Altogether there are at least 40 elements with bcc as their high-temperature phase.[1] Friedel[2] has recently discussed 18 of these, all close packed at low temperatures, in terms of a specific vibrational model. Furthermore, Hoover, Young, and Grover[3] have shown that interatomic-potential models of the form r^{-n} ($n \leq 7$) have a stable high-temperature bcc phase.

Studies of homogeneous crystal nucleation also indicate that bcc is favored. An elegant series of experiments by Cech[4] investigated the rapid cooling of a Fe-Ni molten alloy and showed that, although the stable crystalline structure was fcc at all temperatures, the first phase formed was always (metastable) bcc. Likewise, recent molecular-dynamics (MD) studies of freezing of a Lennard-Jones fluid by Mandell, McTague, and Rahman[5] found that, although nucleation occurred only with difficulty, the initial crystalline phase was bcc, even though fcc is the stable form for this potential. More recent MD work[6] on a pseudopotential for Rb shows that in this case, for which bcc is the stable structure, nucleation oc-

curs with great ease. There is thus strong evidence that bcc is favored by a universal factor.

There are also indications that noncrystalline solids, presumably representing situations where crystal nucleation was inhibited, tend to have icosahedral local structure. Barker, Hoare, and Finney[7] have shown that an amorphous Lennard-Jones packing has about 32% of its atoms in icosahedral sites, while Briant and Burton[8] have noted that the scattering patterns observed in various amorphous metals such as NiP, $Ni_{32}Pd_{53}P_{15}$, PdSi, and CuMg are quite similar to those from icosahedral clusters and qualitatively dissimilar to microcrystalline interference functions.

We show here that these results (and, we believe, many others) can be understood from very general symmetry considerations of the liquid-to solid-phase transition. A straightforward extension of Landau's analysis[9] leads to the conclusion that bcc should be favored near the melting line when the first-order character of the transition is not too pronounced. This is presumably the case in the metals which have a small volume change on crystallization, and a heat of transition less than kT (ΔH for the rare gases and other elements on the right-hand side of the periodic table is greater than kT; so one does not expect Landau theory to be reliable for these systems). It also explains both the preference for bcc in nucleation and the appeareance of icosahedral arrangements when bcc is inhibited, e.g., by density considerations. In two dimensions the same analysis predicts triangular (or honeycomb) structures. This is a necessary conclusion, since these transitions are at most weakly first order. Here the results are, of course, less surprising as this is also the close-packed structure. We

also show that, because of the Brazovskii effect,[10] freezing from a liquid with full rotational symmetry is always a first-order transition for any dimensionality.

Consider the Landau expansion of the free energy near the isotropic phase:

$$\Phi = \Phi_2 + \Phi_3 + \Phi_4 + \cdots . \tag{1}$$

Here φ is the free energy of a system subject to the constraint of periodic density waves, relative to the free energy F_0 of the liquid in the absence of such constraint. F_0 includes the naturally occurring short-range correlations of the normal liquid state.

The quadratic term has the form

$$\Phi_2 = \int d^3q \, A_q \rho_{\vec{q}} \rho_{-\vec{q}}, \tag{2}$$

where $\rho_{\vec{q}}$ is the Fourier component of the density. In an isotropic system A_q can depend only on the magnitude of $\vec{q}$. Near a phase transition A_q will have a minimum at some wave vector Q; so the order parameter is associated with an irreducible representation of the rotational group described by the sphere of radius Q. Clearly the contribution of the order parameter to Φ_2 depends only on the magnitude of

$$\rho_Q{}^2 = \int d\Omega_{\vec{Q}} \, \rho_{\vec{Q}} \rho_{-\vec{Q}}, \tag{3}$$

and is therefore independent of the specific combination of $\rho_{\vec{Q}_i}$.

Consider, however, the third-order term Φ_3. On the sphere it must be of the form

$$\Phi_3 = B_Q(T, P) \iiint d\Omega_1 \, d\Omega_2 \, d\Omega_3 \, \delta(\vec{Q}_1 + \vec{Q}_2 + \vec{Q}_3) \rho_{\vec{Q}_1} \rho_{\vec{Q}_2} \rho_{\vec{Q}_3}, \tag{4}$$

constraining the $\vec{Q}_1$ to form an equilateral triangle.[9] Thus, since $\rho_{-\vec{Q}} = \rho_{\vec{Q}}{}^\dagger$ a nonvanishing contribution to Φ_3 requires at least three $\rho_{\vec{Q}_i}$ (and three $\rho_{-\vec{Q}_i}$) in the order parameter

$$\rho_Q(\vec{r}) = \frac{1}{\sqrt{2}} \sum_{i=1}^{n} [\rho_{\vec{Q}_i}(\vec{r}) + \rho_{-\vec{Q}_i}(\vec{r})], \quad n \geq 3. \tag{5}$$

In order to maximize Φ_3 at fixed $|\rho_Q|^2$ one requires equal amplitudes of the n (≥ 3) pairs $\vec{Q}_i$, $-\vec{Q}_i$:

$$n|\rho_{\vec{Q}_i}|^2 = \rho_Q{}^2. \tag{6}$$

The number of terms in Φ_3 is $2n/3$ if each Q_i appears once and $4n/3$ if it appears twice. Thus we

have the relationship

$$\Phi_3 \sim \rho_Q{}^3 n^{-1/2}, \tag{7}$$

and only closed configurations with finite n are of interest. One can use standard group-theoretical methods to find the point groups which are consistent with this; a more graphic method is to examine the regular polyhedra formed from identical equilateral-triangular faces.

The simplest case is the triangle itself, $n = 3$. Here the order parameter is

$$\rho_Q(\vec{r}) = \pm(\tfrac{2}{3})^{1/2}[\cos QX + 2\cos\tfrac{1}{2}QX \cos\tfrac{1}{2}\sqrt{3}QY], \tag{8}$$

giving

$$|\Phi_3{}^{\text{hex}}| = 2B\rho_Q{}^3/3\sqrt{3}. \tag{9}$$

This is the only two-dimensional case and, depending on the sign in $\rho_Q(\vec{r})$, corresponds to either a (positive) triangular structure or its (negative) conjugate, the honeycomb lattice. In three-dimensional space these give rodlike structures with two-dimensional periodicities, as observed for lyotropic mesophases.

With $n = 6$ the triangles can be arranged to form an octahedron, with

$$\rho_Q(\vec{r}) = \frac{2}{\sqrt{3}} \rho_Q[\cos\tfrac{1}{2}\sqrt{2}QX \cos\tfrac{1}{2}\sqrt{2}QY + \cos\tfrac{1}{2}\sqrt{2}QX \cos\tfrac{1}{2}\sqrt{2}QZ + \cos\tfrac{1}{2}\sqrt{2}QY \cos\tfrac{1}{2}\sqrt{2}QZ], \tag{10}$$

and

$$\Phi_3{}^{\text{bcc}} = 4B\rho_Q{}^3/3\sqrt{6}. \tag{11}$$

The reciprocal lattice formed by the six pairs of $\vec{Q}_i$ is face-centered cubic, with a body-centered direct lattice. Note also that the coefficient of $B\rho_Q{}^3$ is larger for bcc than for the two-dimensional lattice, favoring the former structure.

There is only one structure that displays a more intricate symmetry than the cubic group, namely the icosahedron (and its conjugate the dodecahedron). The $\vec{Q}_i$ are then parallel to the edges of the icosahedron, giving $n = 15$, and

$$\Phi_3{}^{icos} = 4B\rho_Q{}^3/3\sqrt{15}. \qquad (12)$$

Thus, $\Phi_3{}^{icos}/\Phi_3{}^{bcc} = (\frac{2}{5})^{1/2}$. Of course, the regular icosahedron, with its fivefold axis, cannot form a periodic structure.[10] We thus conclude that the bcc structure is uniquely favored by the third-order terms. Note that, e.g., fcc fluctuations ($n = 4$) have no Φ_3. Specific structures other than bcc (or local icosahedral) require higher-order terms.

We consider then Φ_4, which is of the general form

$$\Phi_4 = \int [\prod_{i=4}^{4} d^3Q_i\, C(\vec{Q}_i)]\rho_{\vec{Q}_1}\rho_{\vec{Q}_2}\rho_{\vec{Q}_3}\rho_{\vec{Q}_4}\delta(\sum_i \vec{Q}_i),$$

$$\text{with } |\vec{Q}_i| = Q. \qquad (13)$$

Since the Q_i must form a closed (in general nonplanar) quadrangle $C(\vec{Q}_i)$ can then depend only on the two independent internal angles, say θ_{12} ($=\theta_{34}$) and θ_{14} ($=\theta_{23}$). Because of these degrees of freedom Φ_4 can depend on specific features, such as bond angles, packing considerations, and band structure. For sufficiently large ρ_Q these effects can, of course, dominate. The mechanism favoring the bcc and icosahedral structures is, however, universal, model independent, and qualitatively different from those which favor other phases. Now, the only universal thermodynamic quantity in the problem is the entropy of ordering. It thus follows that entropy considerations will quite generally favor the bcc phase over all other crystal classes. This symmetry is the "natural" solid structure and should dominate near the isotropic liquid phase as long as specific forces are not too strong. This is a generalization of the conclusion of Friedel[2] and of Hoover, Young, and Grover[3] for specific dynamical models.

One can now construct a generalized phase diagram. It is clear that the Landau expansion favors the bcc phase in the region of the melting line so long as the first-order character of the transition is sufficiently weak. These considerations can be made more concrete by considering the vicinity of the Landau critical point where, in mean-field approximation, the liquid-solid transition would be predicted to be second order. This point, denoted (C) in Fig. 1, is defined by the conditions $A_Q = B_Q = 0$, and $\Phi_4 > 0$ for all solid
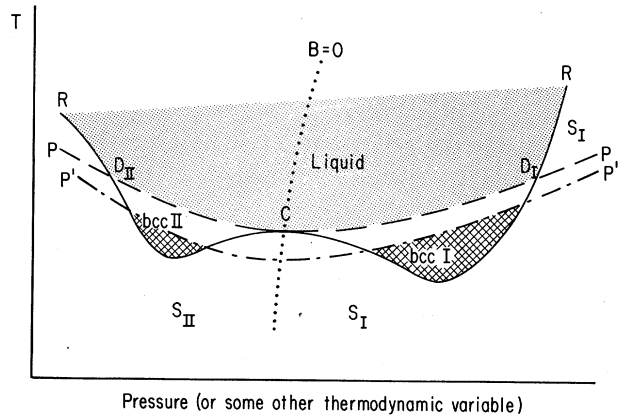

FIG. 1. Schematic generalized phase diagram in the vicinity of a Landau solid-liquid critical point C. Below the solid line R, phases S_I and S_{II} are stable, while in mean field, bcc is stable relative to the liquid, below P. When fluctuations are taken into account, the line P is lowered to P', eliminating the critical point.

structures. In the vicinity of C the (mean-field) phase diagram will then have the general form shown in Fig. 1, where the two conjugate bcc phases correspond to $B \gtrless 0$, and S_I and S_{II} are two other specific phases (favored by Φ_4) which may or may not differ in symmetry when the sign of B changes. $B > 0$ gives the normal bcc structure, with atoms at cube corners and center, while $B < 0$ has atoms at the interstices of this. The unfavorably low density of the latter (for given nearest-neighbor separation) makes it unlikely that this region of the phase diagram can be reached with realistic thermodynamic parameters. In mean field, then, a continuous transition from the liquid (L) to S is possible at C, but not in its immediate vicinity, because there $B \neq 0$ but Φ_4 is still positive. The bcc S phase boundary (R) can, however, cross the (bcc) melting curve P at points D far from C, where the transition is strongly first order. In mean field, one thus predicts stable bcc pockets if at least one of the points D is within the physically accessible range. On the melting line $RDCDR$ the bcc is stable only between D_I and D_{II}. Thus, despite the fact that small bcc fluctuations are always favored in the liquid, mean-field theory predicts that these fluctuations cannot nucleate a metastable bcc phase in the regions RDP, where only S is stable. One can, of course, still nucleate the bcc phase if one supercools the liquid to below the line P, where bcc becomes stable with respect to the liquid, but only metastable relative to S.

The phase diagram is modified in an important way when fluctuations are taken into account. For a rotationally symmetric liquid the fluctuations in $\rho_{\vec{q}}$ above the transition depend only on the magnitude of q and thus have a one-dimensional dispersion. They depend only on $|q| - Q$. As shown by Brazovskii,[11] it follows that the continuous transition (predicted at C or in two dimensions) does not occur, because it would imply diverging fluctuations $\langle \rho^2 \rangle$ as the transition is approached from above. As a result the transition is shifted downwards and is always first order, independent of dimensionality, provided that there is a divergent susceptibility for the field conjugate to the order parameter. The possibility of a liquid-solid critical point is thus eliminated. We have drawn the shifted phase boundary (P') schematically as a dash-dotted line in Fig. 1. Note that the single point C is now replaced by a segment (along this line P') of weakly first order L-S transitions. Below this line the bcc phase is essentially stable, compared to the liquid (but of course less stable than S). If the downward shift is sufficiently large the bcc pockets would completely disappear as thermodynamically stable phases. Thus one could have a segment of the phase boundary where one can nucleate metastable bcc structures even where there are no stable bcc phases and without drastic supercooling.

We would like to thank P. Pincus for encouragement, illuminating discussions, and help in bringing the authors together. One of us (S.A.) thanks both R. Orbach for bringing Ref. 2 to his attention, and the patient students of a seminar for giving him the opportunity to sort out the Landau theory for this problem. One of us (J.P.M.) thanks A. Rahman for sharing his insight and enthusiasm. This work was supported in part by the National Science Foundation, Grants No. CHE76-21293 and No. DMR75-19544 and the U. S. Office of Naval Research, Contract No. N0014-75-C-0245 P3.

(a) Permanent address: The Racah Institute of Physics, The Hebrew University, Jerusalem.

[1] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974).

[2] J. Friedel, J. Phys. Lett. (Paris) 35, 159 (1974).

[3] W. G. Hoover, D. A. Young, and R. Grover, J. Chem. Phys. 56, 2207 (1972).

[4] R. E. Cech, Trans. AIME. J. Metals 206, 535 (1956).

[5] M. J. Mandell, J. P. McTague, and A. Rahman, J. Chem. Phys. 66, 3070 (1970).

[6] C. S. Hsu and A. Rahman, unpublished; J. Maguire and J. P. McTague, unpublished.

[7] J. A. Barker, M. R. Hoare, and J. L. Finney, Nature (London) 257, 120 (1975).

[8] C. L. Briant and J. J. Burton, J. Chem. Phys. 63, 2045 (1975); C. L. Briant, Disc. Faraday Soc. 61, 25 (1976).

[9] L. D. Landau, Phys. Z. Sowiet 11, 26, 545 (1937) [*The Collected Papers of L. D. Landau*, edited by D. ter Haar (Gordon and Breach-Pergamon, New York, 1965), p. 193].

[10] We are aware of two additional possibilities with $n = 15$; a cubic point ($\varphi_3 \propto 8/5\sqrt{15}$), and a D_{10h} line. Both seem of little physical interest.

[11] S. A. Brazovskii, Zh. Eksp. Teor. Fiz. 68, 42 (1975) [Sov. Phys. JETP 41, 85 (1975)]; S. A. Brazovskii and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. 69, 979 (1975) [Sov. Phys. JETP 42, 497 (1976)].

Crossover in the Dynamic Exponent z for Three-Dimensional Ferromagnets

Robert M. Suter and Christoph Hohenemser

Department of Physics, Clark University, Worcester, Massachusetts 01610

(Received 19 May 1978)

For isotropic three-dimensional ferromagnets, neutron-scattering and hyperfine-interaction experiments yield 2.5 and 2.0, respectively, for the dynamical critical exponent z. This apparent contradiction is removed by two hypotheses. (1) The effective value of z depends on the wave-vector region sampled, and for small q approaches $z = 2.0$. (2) Hyperfine-interaction experiments are asymptotic in q, while present neutron-scattering experiments are not.

Near a magnetic critical point, the spin-spin correlation function for the ith spin component, $S^{ii}(\vec{q}, \omega)$, depends on three critical exponents, η, ν, and z. According to current theory, the static exponents η and ν are universal within a class of systems having the same lattice dimensionality, d, and spin dimensionality, N; the dynamic exponent, z, depends in addition on the conservation laws describing the motions of the spins.[1] Since $S^{ii}(\vec{q}, \omega)$ is proportional to the cross section for