Theory and Model for Martensitic Transformations

Per-Anker Lindgård
Risø National Laboratory, DK-4000 Roskilde, Denmark
and
Ole G. Mouritsen
Department of Structural Properties of Materials, The Technical University of Denmark, DK-2800 Lyngby, Denmark
(Received 21 July 1986)

Martensitic transformations are shown to be driven by the interplay between two fluctuating strain components. No soft mode is needed, but a central peak occurs representing the dynamics of strain clusters. A two-dimensional magnetic-analog model with the martensitic-transition symmetry is constructed and analyzed by computer simulation and by a theory which accounts for correlation effects. Dramatic precursor effects at the first-order transition are demonstrated. The model is also of relevance for surface reconstruction transitions.

PACS numbers: 81.30.Kf, 64.60.Fr, 75.40.Fa

Most metals that are closed packed at low temperature undergo at higher temperature a structural transition to a bcc structure.[1] This is called a martensitic transformation. In spite of its universality there does not exist a theory which in a satisfactory way explains this transition. We shall here argue that it is strain fluctuations caused by the anharmonicity which drives the transition and that therefore linear or harmonic theories will fail. The problem is mapped onto a two-dimensional magnetic lattice model and we investigate this by correlation theory[2] and Monte Carlo computer simulation. The lattice model allows an extensive simulation study of large systems, much larger than is possible with molecular dynamics on systems with translational degrees of freedom.[3] This is of decisive importance for an investigation of fluctuation effects and the correlation length of short-range order. The model by itself has a wide range of possible applications ranging from physisorbed overlayers, surface reconstructions, and structural polytypism to martensitic transformations, of which only the latter will be considered here.

The early theory by Zener[4] suggested that a softening of a shear mode in the bcc phase causes the martensitic transition. However, except for Li and Na the shear constant $c=(c_{11}-c_{12})/2$ is not very small and no evidence for a softening has in general been observed.[5] This led Friedel[5] to suggest that, since the transition occurs at temperatures higher than the Debye temperature, the excess entropy for the bcc phase is due to an overall lower photon spectrum, expected to scale with the number of neighbors, eight for bcc and twelve for hcp. A direct quasiharmonic calculation of the vibrational free energy for the bcc and hcp phases for Zr, with use of the recently measured phonon dispersion curves in both phases,[6] is now possible. It was recently pointed out by Watson and Weinert[7] that the electronic entropy difference is of the order of $0.2k_B$ and not negligible. For Zr the calculated quasiharmonic vibrational plus the electronic free energy is found[8] to be identical for the bcc and the hcp phases within the error limits set by the accuracy of a fit to the measured phonons, close to the martensitic transformation at $T_M=1135$ K. The conclusion is that the effects considered previously are important in making the transition possible, but do not cause it as such and do not give an understanding of the transition mechanism. Neither is a soft mode observed as required for the Zener single-strain theory. A similar situation exists for Na[9] and Tl.[10]

Let us now in Fig. 1 consider a physical picture of the martensitic transition following the Nishiyama-Wassermann rule,[1] which transforms the planes $(110)_{bcc}\rightarrow(111)_{fcc}$ and the directions $[1\bar{1}0]_{bcc}\rightarrow[1\bar{2}1]_{fcc}$ for the bcc$\rightarrow$fcc transition and similarly $\rightarrow(0001)_{hcp}$ and $\rightarrow[1\bar{1}00]_{hcp}$ for the bcc$\rightarrow$hcp transition. The latter will be discussed here. It occurs in Zr and many other metals and alloys.[1] We need in the bcc phase two strains: a uniform strain $\varepsilon_1\{001\}\langle001\rangle$ along $z=[001]_{bcc}$ reducing the angle $\theta_c=125.3°$ to $\theta_h=120°$ thereby making perfect hexagons, and the internal shear strain $\varepsilon_2\{110\}\langle1\bar{1}0\rangle$ along $x=[1\bar{1}0]_{bcc}$ shuffling atoms in every second layer

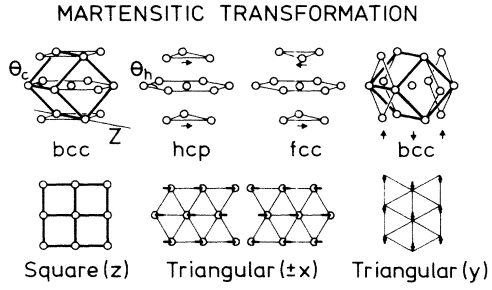

FIG. 1. Top left: The near-hexagonal planes in the bcc structure, but with $\theta_c=125.3°$. A ε_1 strain along $z=[001]$ gives perfect hexagons with $\theta_h=120°$. By shuffling atoms in every second plane by a ε_2 strain as indicated by arrows we obtain the hcp or fcc structures. A second of the six possible equivalent domains is shown to the right. Lower part: A projection along [001] with the atomic movements represented by spins on a square lattice. The magnetic model with ferromagnetic and antiferromagnetic order is represented by the Hamiltonian (3).

into the hcp positions. ε_1 has the same elastic constant c as the shear mode of ε_2 symmetry considered by Zener. Here ε_2 is the internal strain corresponding to the low-frequency transverse N-point phonon mode T_1 measured in Zr at $\omega_N = 1$ THz. The stability of the bcc phase can be evaluated by a Landau expansion of the free energy in terms of these strains. The symmetry allows then the following terms:

$$F = F_0 + \tfrac{1}{2}c\varepsilon_1^2 + \tfrac{1}{2}\omega_N\varepsilon_2^2 + V_3\varepsilon_1\varepsilon_2^2 + V_4\varepsilon_2^4 + V_4'\varepsilon_1^4. \quad (1)$$

The V_3 term couples the uniform strain with two internal strains. The anharmonic terms V_n are not expected to vary rapidly with temperature near T_M. F_0 is the quasiharmonic vibrational and electronic free energy, assumed to be the same for the bcc and hcp structures, as found above. Minimization of F with respect to ε_1 gives

$$F = F_0 + \tfrac{1}{2}\omega_N\varepsilon_2^2 + [V_4 - V_3^2/c]\varepsilon_2^4 + V_6\varepsilon_2^6. \quad (2)$$

A small c may then cause the effective fourth-order term $V_{4\text{eff}}$ to be negative and consequently give rise to a first-order martensitic transition, as observed. We emphasize that neither ω_N nor c need vanish as required by the Zener theory, but the transition is a consequence of the interplay between two strains.[11] Only a small softening of ω_N is required, and it is important to note that this does not necessarily imply that the observed N-point phonon mode softens significantly, as discussed below.

In an earlier study[12] of the Bain bcc↔fcc transition an analysis was made which also led to the identification of strains of the ε_1 and ε_2 symmetry as the most important strain components. However, since only the uniform strain of ε_2 symmetry and only second-order coupling terms in the energy expansion were considered, the importance of the *internal* ε_2 strain was not recognized and a low-energy path along ε_1 was suggested. The result of the couplings in (1) suggests that the lowest free-energy path between the bcc and hcp structures occurs in the $\varepsilon_1,\varepsilon_2$ space along a valley with minima and saddle point along the parabolic path $\varepsilon_1 = (V_3/c)\varepsilon_2^2$. The free energy along this path is given by (2). Possible third-order terms[13] $V_3'\varepsilon_1^3$ and higher-order coupling terms in (1) may modify this path slightly, as may also coupling to the volume strain, which was shown[12] to renormalize c.

To substantiate the simple two-strain theory we study a specific microscopic interaction model by computer simulation and correlation theory.[2] In both cases it is most convenient to represent the atomic motion by a spin located at the average position. The model thus excludes atomic diffusion, which as a characteristic fact is found not to play a role at the martensitic transformation,[1] which is dominated by large shears as emphasized in the model. To simplify further let us consider only a projection on the $(001)_{\text{bcc}}$ plane, which is shown as a two-dimensional square lattice in the lower part of Fig. 1. The uniform ε_1 strain is represented by a ferromagnetic order in the z direction perpendicular to the plane (we call this the square phase) and the internal strain ε_2 is represented by an antiferromagnetic structure with the moment in either the x or the y direction in the xy plane (we call this the triangular phase). The real bcc→hcp transition has of course lattice dimension $d = 3$ and six hcp domains, two for each equivalent $[1\bar{1}0]_{\text{bcc}}$ direction. The magnetic model that we consider has the same symmetry, but with $d = 2$ and an $n = 2$ component order parameter in the triangular phase corresponding to four antiferromagnetic domains. The two-dimensional nature enhances the fluctuation effects we are to discuss. The model is obviously of direct relevance for the surface reconstruction problem as found, e.g., on the W(001) surface.[14] The following magnetic Hamiltonian stabilizes the ferromagnetic and antiferromagnetic order according to the relative strength of the Ising interaction K and the two-dimensional, pseudodipolar interaction J:

$$H = \sum_{ij}\{-KS_{iz}S_{jz} + J[\mathbf{S}_i\cdot\mathbf{S}_j - P(\mathbf{r}_{ij}\cdot\mathbf{S}_i)(\mathbf{r}_{ij}\cdot\mathbf{S}_j)]\} + H_c, \quad (3)$$

with $P = 2$. An anisotropy term $H_c = -D\sum_i(S_{ix}^4 + S_{iy}^4)$ with $D > 0$ breaks the continuous xy degeneracy and stabilizes the x or the y direction. This is convenient for the computer simulations of (3) with classical spins. For $S = 1$ the term reduces exactly to $H_c = D\sum_i S_{iz}^2$ (favoring just the xy plane) and (3) becomes a singlet-doublet model which has previously been intensively studied.[2,15,16] In both cases the transition is from $n = 1$ to $n = 2$, which at the paramagnetic phase boundary gives rise to a bicritical point. The martensitic transformation corresponds to a crossing of the first-order line at T_M.

The phase diagram calculated by computer simulation for classical spins is shown in Fig. 2(a) for $D = 2J$. The simulations are carried out by use of Monte Carlo importance-sampling techniques, and standard methods have been employed to estimate finite-size effects and the order of the phase transitions.[17] The lattice sizes studied range from 20^2 to 100^2 spins and the statistical ensembles incorporate from 10^3 to 10^4 microconfigurations. At T_M there is a finite ferromagnetic magnetization M_z in the square phase. Using the correlation theory we calculate the free energy and consider the influence of a small increment m_z and a small antiferromagnetic order parameter m_x. The free energy assumes exactly the form (1):

$$F = F_0 = (2\chi_u^{zz})^{-1}m_z^2 + (2\chi_s^{xx})^{-1}m_x^2 + V_4m_x^4 + V_3m_zm_x^2 + \ldots, \quad (4)$$

from which (2) follows, giving a first-order transition if $V_4^{\text{eff}} = V_4 - \chi_u^{zz}V_3^2 < 0$. V_3 is finite for finite M_z, but vanishes in the paramagnetic phase. V_3 and V_4 vary slowly with temperature and are reasonably accurately given simply by mean-field theory. χ_u^{zz} is the uniform and χ_s^{xx} the staggered susceptibility for finite M_z. For these sus-

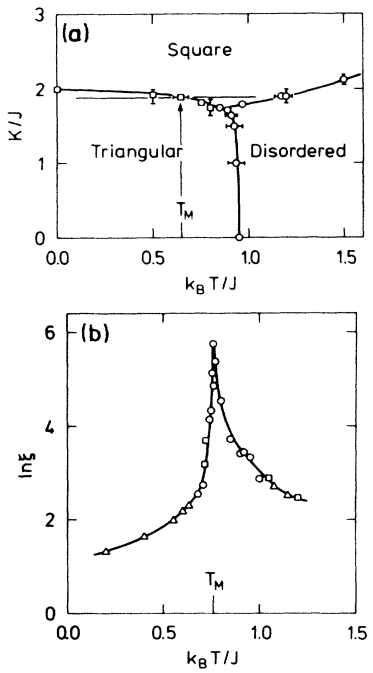

FIG. 2. (a) Phase diagram and (b) correlation length ξ (in units of a/π, $a=1$) determined by computer simulation for the magnetic model (3) of a first-order martensitic transformation at T_M ($K/J=1.8$). ξ is calculated by fitting of the first and second q moments to those of a cutoff Lorentzian structure factor. Strong precursor phenomena at the first-order transition are found, caused by correlation effects.

ceptibilities it is important to include correlation effects, which give rise to a rapid temperature variation. In the correlation theory[2,15] these are calculated by a mode-mode-coupling approximation. For wave-vector-dependent fluctuations $m_z(q)$ and $m_x(q)$ we find the inverse susceptibility components $1/\chi_u^{zz}(q)=R_z-K\gamma_q \sim \kappa_z^2+q^2$ and $1/\chi_s^{xx}(q)=R_x-J\gamma_q\sim\kappa_x^2+q^2$ with $\gamma_q=2\times(\cos q_x+|\cos q_y|)$ where $\mathbf{q}$ is measured from the ferromagnetic or antiferromagnetic zone center for z and x, respectively. If we include only the most dominant fluctautions we find the local inverse susceptibility $R_z=C_2/C_1$, where $C_n=J^n\sum_q\gamma_q^n\langle m_x(q)m_x(-q)\rangle$. C_1 is proportional to the nearest-neighbor correlation function. C_2 involves both the self-correlation, which varies slowly with temperature, and the next-nearest-neighbor correlation. At high temperature when $\langle m_x(q)m_x(-q)\rangle \sim k_B T\chi_s^{xx}(q)$, we find further that $R_x\sim R_z$. An increasing antiferromagnetic short-range order (i.e., increasing C_1 or correlation length $\xi_x=1/\kappa_x$) is therefore self-reinforcing by making coefficients to both m_x^2 and m_x^4, $1/\chi_s^{xx}$ and V_4^{eff}, smaller and therefore the fluctuations larger. We thus predict a precursory increase of antiferromagnetic short-range order. Precisely analogous arguments can be presented by consieration of the transition from the triangular phase.

By the computer simulation we have calculated the correlation lengths ξ_x and ξ_z for short-range order in the quadratic and triangular phases, respectively. Figure 2(b) shows a dramatic increase in the correlation lengths upon approach to the first-order transition at T_M from both sides in agreement with the above analysis. The effect is of course particularly large for the considered two-dimensional case, but expected qualitatively also in three dimensions. We have used $P=2$ in (3) which gives isotropic triangular short-range order in the plane. A value $P\neq 2$ will give more realistic streaklike fluctuations expected for the martensitic transformation.[18]

Finally a remark about soft-mode frequencies. An exact sum rule gives for the first-moment frequency $\langle\omega_q\rangle=M_z[\chi_s^{xx}(q)\chi_s^{yy}(q)]^{1/2}$. If the spectrum is assumed to be quasiharmonic, i.e., a δ-function response at $\omega_q^H=\langle\omega_q\rangle$, we must in conjunction with the increased short-range order observe a softening of ω_q^H. However, this is not the case in the presence of significant damping. For the $S=1$ singlet-doublet model[2] and the antiferromagnet,[15] it was shown that in the presence of two dynamical variables the spectrum develops a central peak at $\omega=0$, in addition to a broadening peak at ω_q^{peak} near ω_q^H when $\langle\omega_q\rangle$ decreases. Now, ω_q^{peak} does not vanish, but loses intensity to the central peak, which increases proportionally to χ_s^{xx}. The same situation is expected for the real bcc$\rightarrow$ hcp martensitic transformation and ω_N in (1) must be identified with $\langle\omega_q\rangle$, and not ω_q^{peak}. Since $T_M\gg\theta_{\text{Debye}}$ there are strong interactions between the phonons, and the quasiharmonic description of the phonons is unsatisfactory. In analogy with the magnetic case we thus predict that when the precursory short-range order begins to develop, a finite-width central peak emerges in the phonon spectrum. Such an effect has previously been discussed for other structural phase transitions.[19] The physical interpretation of this is the temporal evolution of clusters of the hcp phase in the bcc phase and vice versa. The width is expected to be overestimated in the simple pair mode-mode-coupling theory.[2,15] In Zr there was in fact observed[6b] a relatively high-intensity quasielastic scattering. It was cautiously attributed to other effects[6b] and a further study of the temperature dependence would be valuable to clarify its role for the transition. An intensity loss without softening of the phonon spectrum was reported for Na.[9] There is considerable evidence from electron microscopy and x-ray diffraction[18] that fluctuating $\varepsilon_2\{110\}\langle 1\bar{1}0\rangle$ shears are characteristic of the initial step in the formation of martensite in most systems. This is in accordance with the present theory and model. Usually the premartensitic fluctuations are observed, also by neutron scattering,[19] to occur slightly incommensurate relative to the parent lattice. Such an effect could be accounted for in the model by our allowing farther-neighbor interaction in (3). The computer simulation presented here demonstrates the presence and growing importance of short-range order clusters near T_N. The kinetics of the cluster formation is found to be very slow.

Above we have discussed a theory and magnetic analog of the bcc-hcp transition as it occurs for example in Zr, Tl, Na, etc. More complicated closed-packed structures exist with long-range ordered stacking faults. Several aspects of the stability of these structures in insulators can be described[20] by the axial next-nearest-neighbor Ising model, although it appears to be less applicable for metallic systems.[21] The two-dimensional magnetic Heisenberg-like model considered here, when extended to include next-nearest-neighbor interactions and $P \neq 2$, is still simple, but more realistic allowing also a calculation of the dynamic behavior. For the transition to the long-range hexagonal structures we again need two dynamical variables, i.e., the two strains, ε_1, and a shuffling strain, $\varepsilon_2(Q)$, now with a shorter wave vector, $0 < Q < \pi$. The free energy again assumes the form (1) and the correlation theory predicts a central peak indicating that fluctuations are driving the transition rather than a softening of the phonon spectrum.

In conclusion, the martensitic transformation is a high-temperature transition in which the anharmonic phenomena play the important role of giving rise to precursor phenomena in both static and dynamic properties. Linear and quasiharmonic theories are inadequate for describing this.

This work was supported by the Danish Natural Science Research Council under Grants J.No. 11-5176 and 5.21.99.72. We thank B. N. Harmon for stimulating discussions, B. R. Cooper for friendly advice, and P. C. Clapp for useful correspondence.

[1]Z. Nishiyama, *Martensitic Transformations* (Academic, New York, 1978).

[2]P.-A. Lindgård, Phys. Rev. Lett. **50**, 690 (1983), and J. Magn. Magn. Mater. **52**, 47 (1985), and **54**, 1227 (1986).

[3]G. De Lorenzi and C. P. Flynn, J. Phys. C **18**, L769 (1985).

[4]C. Zener, Phys. Rev. **71**, 846 (1947).

[5]J. Friedel, J. Phys. (Paris), Lett. **35**, L59 (1974).

[6a]C. Stassis, J. Zaretsky, and N. Wakabayashi, Phys. Rev. Lett. **41**, 1726 (1978); C. Stassis, J. Zaretsky, D. Arch, O. D. McMasters, and B. N. Harmon, Phys. Rev. B **18**, 2632 (1978).

[6b]C. Stassis and J. Zaretsky, Solid State Commun. **52**, 9 (1984).

[7]R. E. Watson and M. Weinert, Phys. Rev. B **30**, 1641 (1984).

[8]Y.-Y. Ye, Y. Chen, K. M. Ho, B. N. Harmon, and P.-A. Lindgård, to be published.

[9]G. Dolling, B. M. Powell, and P. Martel, Can. J. Phys. **46**, 1727 (1968); R. Stedmann, J. Phys. F **6**, 2239 (1976).

[10]M. Iizumi, J. Phys. Soc. Jpn. **52**, 549 (1983).

[11]The first-order transition occurs approximately when $\omega_N = \frac{1}{2} V_{4\text{eff}}^2 / V_6$; the barrier height is then $\Delta F = \frac{2}{27} \omega_k^2 / V_{4\text{eff}}$. From the path condition, $V_3/c = \varepsilon_1/\varepsilon_2^2|_{\text{hcp}}$ and thus V_3 can be eliminated from $V_{4\text{eff}}$ (2). Here we only consider the bicritical case $V_4 V_4' M_z^2 < V_3^2$. For the tetracritical case $V_4 V_4' M_z^2 > V_3$ there exists a mixed phase with both strains ε_1 and ε_2 finite, as discussed by F. Wegner, Solid State Commun. **12**, 785 (1973); P.-A. Lindgård, Phys. Rev. B **14**, 4074 (1976).

[12]P. Beauchamp and J. P. Villain, J. Phys. (Paris) **44**, 1117 (1983); their η_1 and η_3 are uniform strains of ε_1 and ε_2 symmetry.

[13]P. C. Clapp, Phys. Status Solidi (b) **57**, 561 (1973).

[14]D. A. King, Phys. Scr. **T4**, 34 (1983); M. Weinert, A. J. Freemann, and S. Ohnishi, Phys. Rev. Lett. **56**, 2295 (1986).

[15]P.-A. Lindgård, Phys. Rev. B **30**, 2729 (1984).

[16]B. R. Cooper, in *Magnetic Properties of Rare Earth Metals,* edited by R. J. Elliott (Plenum, New York, 1972), p. 17.

[17]O. G. Mouritsen, *Computer Studies of Phase Transitions and Critical Phenomena* (Springer, Heidelberg, 1984).

[18]L. E. Tanner, A. R. Pelton, and R. Gronsky, J. Phys. (Paris), Colloq. **43**, C4-169 (1982).

[19]S. M. Shapiro, Metall. Trans. **12A**, 567 (1981).

[20]J. Smith, J. Yeomans, and V. Heine and other papers in *Modulated Structure Materials,* edited by T. Tsakalakos (Nijhoff, Leiden, 1984), p. 95.

[21]R. Bruinsma and A. Zangwill, Phys. Rev. Lett. **55**, 214 (1985).