PHYSICAL REVIEW B VOLUME 20, NUMBER 7 1 OCTOBER 1979

Theory of order-disorder transitions in the graphite intercalation compounds C_8Cs, C_8Rb, and C_6Li

Per Bak
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

Eytan Domany
Department of Physics, University of Washington, Seattle, Washington 98195

(Received 3 May 1979)

The order-disorder transitions in the stage-1 graphite intercalation compounds C_8Cs, C_8Rb, and C_6Li are analyzed within a Landau-Ginzburg theory. The transitions are all found to be first order, but for different reasons: In C_8Cs the Landau expansion includes third-order umklapp terms, whereas in C_8Rb the ordered phase is stablized by sixth-order anisotropy terms. The transition in C_6Li is described by the three-dimensional three-state Potts model, which also contains cubic invariants. Experiments are suggested to test the predictions.

I. INTRODUCTION

Recently, neutron[1] and x-ray scattering[2] investigations of the graphite intercalation compounds C_8Cs and C_8Rb have revealed phase transitions with a number of interesting properties. In this paper, these phase transitions will be analyzed by means of a Landau-Ginzburg theory. We find that the transitions are described by an $n=6$ model and by an anisotropic Heisenberg model, respectively, and that both transitions are of first order. Also, it will be shown that the melting of the Li sublattice in C_6Li is a realization of the three-dimensional three-state Potts model. According to Landau theory the transition is first order, but there are conflicting theories on the critical behavior of this model.

Structurally, the stage-1 intercalated compounds consist of hexagonal graphite layers, with stacking sequence *AAAA*..., between which there are layers of Cs, Rb, or Li atoms. In the high-temperature phase there is no long-range order in the alkaline layer system, but at some temperature T_0 there is a transition into a phase where the alkali atoms form a regular three-dimensional lattice. In the scattering experiments, the formation of this lattice shows up as a new set of Bragg peaks, or satellites. In C_8Cs the transition takes place at $T_0 \simeq 550$ K,[2] in C_8Rb at $T_0 \simeq 750$ K.[1] For both systems, analysis of the diffraction peaks within the layers showed[1-4] that the alkaline atoms form a hexagonal superlattice occupying one quarter of the graphite prismatic sites (Fig. 1). In the absence of interlayer coupling a transition to this 2 × 2 structure was predicted[5] to belong to the universality class of the two-dimensional four-state Potts model,[6] and the transition therefore can be continuous. However, the ordering in both compounds is three dimensional, and the three-dimensional interactions cannot be ignored. Indeed, the transition temperature depends strongly upon the staging, i.e., the distance between the alkaline layers.

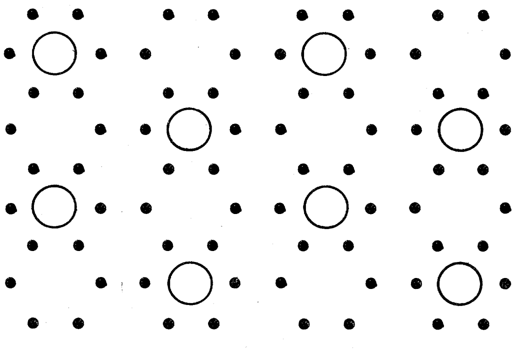

FIG. 1. Intralayer ordering of alkaline atoms in C_8Rb and C_8Cs. The dots represent carbon atoms, and the circles represent the alkaline atoms.

Within each layer the alkali atoms may occupy four symmetric sets of lattice sites, α, β, γ, and δ, corresponding to the four equivalent states in the Potts mode. In the ordered phase of C_8Cs the stacking sequence is $\alpha\beta\gamma\alpha\beta\gamma$..., whereas in C_8Rb the sequence is $\alpha\beta\alpha\beta$... . Our analysis, to be presented in Sec. II, takes into account the full three-dimensional symmetry of the ordered phase.

II. ORDER-DISORDER TRANSITIONS

A. C_8Cs

In the disordered phase the density of Cs atoms is the same at each site. In the ordered phase the density function $\rho(\vec{r})$ has less symmetry since the Cs atoms condense into specific positions. According to the theory of Landau and Lifshitz[7] the phase transition is described by an n-component order parameter transforming as the basis of an n-dimensional irreducible representation of the graphite space group. In general, the representations are labeled with the wave vector giving the periodicity of the ordered phase. The wave vector characterizing the Cs ordering is simply the basis vector of the Cs reciprocal lattice. In terms of graphite reciprocal-lattice vectors $\vec{a}^*$ and $\vec{c}^*$ this is a zone-boundary vector, $\vec{k}_1 = (\frac{1}{2}a^*, 0, \frac{1}{3}c^*)$. The corresponding order parameter, ψ_1, describes a mass density wave[8]

$$\rho_1(\vec{r}) = \psi_1 \exp(i\vec{k}_1 \cdot \vec{r}).$$

The star of $\vec{k}_1$ consists of the six equivalent vectors

$$\pm\vec{k}_1 = (\tfrac{1}{2}a^*, 0, \pm\tfrac{1}{3}c^*) ,$$

$$\pm\vec{k}_2 = (-\tfrac{1}{4}a^*, \tfrac{1}{4}\sqrt{3}a^*, \pm\tfrac{1}{3}c^*) ,$$

and

$$\pm\vec{k}_3 = (-\tfrac{1}{4}a^*, -\tfrac{1}{4}\sqrt{3}a^*, \pm\tfrac{1}{3}c^*) .$$

[See Fig. 2(a).] The order parameter thus has $n = 6$ components, $\psi_{\pm i}$, describing density waves with these six wave vectors.

To verify that the observed $\alpha\beta\gamma$ stacking can indeed be formed by superposition of such waves, and higher harmonics, consider the density function

$$\begin{aligned}\rho(\vec{r}) = {} & \cos\vec{k}_1'' \cdot \vec{r} \left(\cos\frac{2\pi}{3}z - \frac{1}{4}\right) \\ & + \cos\vec{k}_2'' \cdot \vec{r} \left(\cos\frac{2\pi}{3}(z+1) - \frac{1}{4}\right) \\ & + \cos\vec{k}_3'' \cdot \vec{r} \left(\cos\frac{2\pi}{3}(z+2) - \frac{1}{4}\right) + \text{const.} , \qquad (1)\end{aligned}$$

where $\vec{k}_i''$ are the projections of $\vec{k}_i$ on the basal plane. Noting that for $z = 0, 1, 2$ the factor $[\cos(2\pi/3)z - \frac{1}{4}]$ assumes the values $+\frac{3}{4}$, $-\frac{3}{4}$, and $-\frac{3}{4}$, respectively, we find that within each layer the density is given by

$$\rho(\vec{r}) = \tfrac{3}{4}(\pm\cos\vec{k}_1'' \cdot \vec{r} \pm \cos\vec{k}_2'' \cdot \vec{r} \pm \cos\vec{k}_3{}' \cdot \vec{r}) , \qquad (2)$$

where two signs are negative and one is positive. The maxima of the three equivalent functions give the positions of the atoms of the α, β, and γ arrangements.[5]

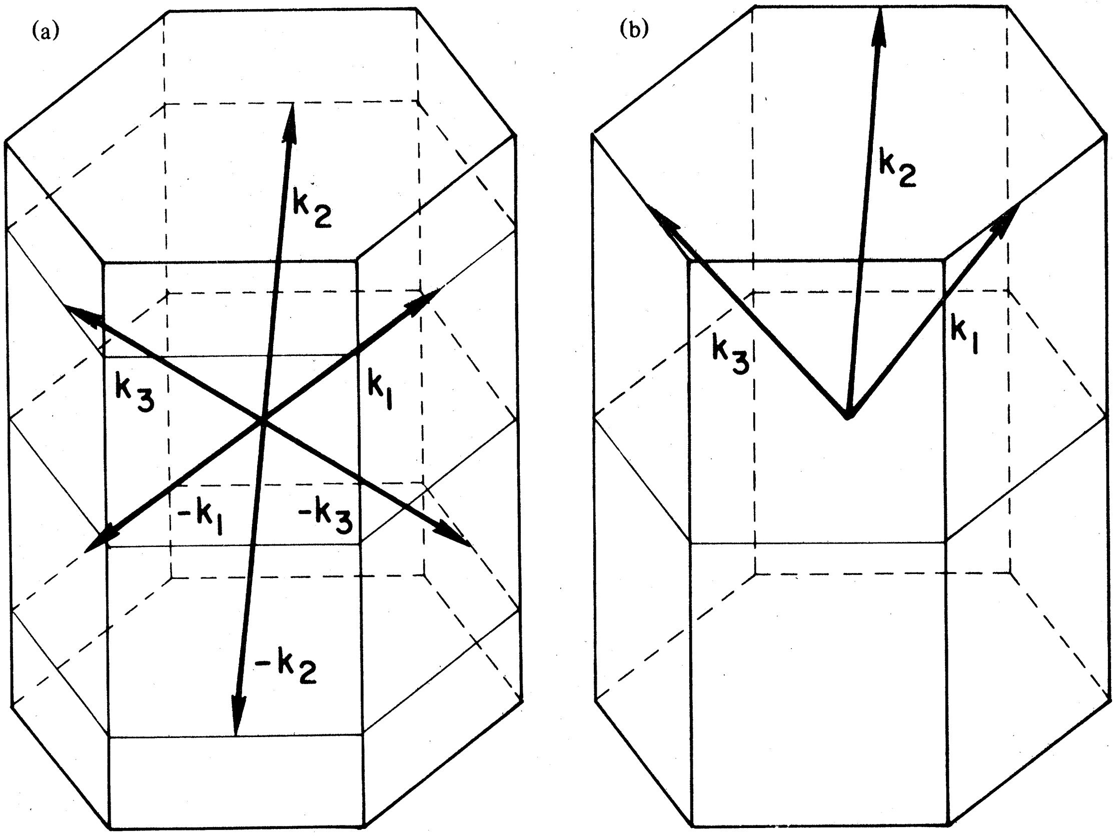

FIG. 2. Brillouin zone for graphite lattice. The vectors shown are the wave vectors characterizing the Cs ordering in C_8Cs (a), and the Rb ordering in C_8Rb (b).

Equation (1) can trivially be rewritten

$$\rho(\vec{r}) = \tfrac{1}{4}\Big[\exp(i\vec{k}_1\cdot\vec{r}) + \exp(-i\vec{k}_1\cdot\vec{r}) + \exp\left(\frac{2\pi i}{3}\right)\exp(i\vec{k}_2\cdot\vec{r})$$
$$+\exp\left(\frac{-2\pi i}{3}\right)\exp(-i\vec{k}_2\cdot\vec{r}) + \exp\left(\frac{4\pi i}{3}\right)\exp(i\vec{k}_3\cdot\vec{r}) + \exp\left(\frac{-4\pi i}{3}\right)\exp(-i\,\vec{k}_3\cdot\vec{r})\Big]$$
$$-\tfrac{1}{8}[\exp(i\vec{k}_1''\cdot\vec{r}) + \exp(i\vec{k}_2''\cdot\vec{r}) + \exp(i\vec{k}_3''\cdot\vec{r})] + \text{const} \ . \tag{3}$$

The first term is clearly a superposition of the six components of the order parameter. The second term is a superposition of three functions transforming as the basis of an $n=3$ irreducible representation lableled by k_1'', k_2'', and k_3''. We are therefore led to introduce order parameters ψ_1'', ψ_2'', and ψ_3'' corresponding to these wave vectors. We shall see that the $n=3$ order parameter is driven by the $n=6$ order parameter.

The Landau expansion of the free energy now takes the form

$$F = \tfrac{1}{2}r\sum_{i=1}^{3}\psi_i\psi_{-i} + u_4\left(\sum_{i=1}^{3}\psi_i\psi_{-i}\right)^2 + v\sum_{i=1}^{3}(\psi_i\psi_{-i})^2$$
$$+u_4'\sum_{i\neq j}(\psi_i^2\psi_{-j}^2) + w(\psi_1\psi_2\psi_3 + \psi_{-1}\psi_{-2}\psi_{-3})$$
$$+u_6'\sum_i(\psi_i^6 + \psi_{-i}^6) + \cdots \ , \tag{4}$$

where the dots represent other sixth-order terms + higher-order terms. We note immediately that the expansion includes a third-order term w. This is due to the fact that the ordering is commensurate in the z direction so that $\vec{k}_1 + \vec{k}_2 + \vec{k}_3$ add up to the reciprocal-lattice vector c^*. Thus, the transition is first order according to one of Landau's rules.[7]

To see that the expansion (4), for proper choice of coefficients, may indeed produce the $\alpha\beta\gamma$ structure (1), consider the situation $w<0$, $u_4'<0$, $u_6'<0$. Inserting $\psi_{\pm j} = A\exp(\pm i\theta_j)$, it is easy to work out that Eq. (4) has extrema for $(\theta_1, \theta_2, \theta_3) = (0, 2\pi/3, 4\pi/3)$. By inspection this gives precisely the phase factors in the first parentheses in Eq. (1). The expansion (3) has 24 equivalent extrema given by $(1/2\pi)(\theta_1, \theta_2, \theta_3) = (0, \frac{1}{3}, \frac{2}{3}), (\frac{1}{2}, \frac{1}{3}, \frac{1}{6})$, $(0, \frac{5}{6}, \frac{1}{6})$, $(\frac{1}{2}, \frac{5}{6}, \frac{2}{3})$ and all possible permutations. This corresponds to the 24 equivalent way of stacking the Cs layers ($\alpha\beta\gamma$, $\beta\gamma\alpha$, $\alpha\beta\delta$, etc.).

Turning now to the $n=3$ parameter ψ_i'', note that it couples to the $n=6$ order parameter $\psi_{\pm i}$ through terms of the form

$$\delta F \simeq (\psi_1\psi_{-2} + \psi_{-1}\psi_2)\psi_3'' + \text{c.p.} \tag{5}$$

The secondary order parameter ψ_i'' is thus induced by the primary order parameter ψ_i. In the absence of the third-order term, $\psi_i'' \sim \psi_i^2$ near T_0. In the experiment[2] this is borne out by the observation that the "(100)" peak [in our notation the $(\frac{1}{2}a^*, 0, 0)$peak] is ten times weaker than the "(101)" peak.

B. C_8Rb

The stage-1 intercalation compound C_8Rb undergoes several consecutive transitions as the temperature is varied.[1] Since most of the transitions were found to be poorly reproducible, we shall concentrate our efforts on the high-temperature transition where the system goes from the disordered phase to the $\alpha\beta\alpha\beta$ phase.

The periodicity of the Rb lattice is given by three equivalent wave vectors

$$\vec{k}_1 = (\tfrac{1}{2}a^*, 0, \tfrac{1}{2}c^*) \ ,$$

$$\vec{k}_2 = (-\tfrac{1}{4}a^*, \tfrac{1}{4}\sqrt{3}a^*, \tfrac{1}{2}c^*) \ ,$$

and

$$\vec{k}_3 = (-\tfrac{1}{4}a^*, \tfrac{1}{4}\sqrt{3}a^*, \tfrac{1}{2}c^*)$$

[see Fig. 2(b)], and therefore the order parameter has three components, ψ_1, ψ_2, and ψ_3. (Note that in the present case $\vec{k}_i$ and $-\vec{k}_i$ differ by a reciprocal-lattice vector.) As before, the lowest harmonics of the mass density wave may be written

$$\rho(\vec{r}) = \delta_1\cos\vec{k}_1''\cdot\vec{r} + \delta_2\cos\vec{k}_2''\cdot\vec{r} + \delta_3\cos\vec{k}_3''\cdot\vec{r} \ , \tag{6}$$

where the product of the signs, $\delta_1\delta_2\delta_3$, equals 1. The $n=3$ representation given by k_1'', k_2'', and k_3'' is induced by the invariant

$$\delta F = \psi_1''\psi_2''\psi_3 + \text{c.p.}$$

The Landau expansion takes the form

$$F = \tfrac{1}{2}r\sum_i(\psi_i)^2 + u_4\left(\sum_i\psi_i^2\right)^2 + v_4\sum_i\psi_i^4$$
$$+u_6\left(\sum_i\psi_i^2\right)^3 + u_6'\sum_i\psi_i^6 + \cdots \ . \tag{7}$$

This is the expansion defining the universality class of the Heisenberg model with cubic anisotropy. A system described by this model might, in principle, exhibit a second-order transition. In the present case, however, the observed structure (6) corresponds to $\psi_2 = \psi_3 \neq 0$, $\psi_1 = 0$. In a (ψ_1, ψ_2, ψ_3) coordinate system, the order parameter points to one of the equivalent centers of the cube edges, (0,1,1). At a second-order transition the direction of the order parameter is given by the fourth-order term. The fourth-order term favors an order parameter in *either* the [100] or the [111] direction. Hence, in our case the transition must be driven by negative higher-order terms (for example, a sixth-order term), and the transition is of first order! Note that this prediction is based on the Landau theory. It is possible that a more refined renormalization-group theory might change our conclusion.

C. C_6Li

At room temperature the Li atoms in C_6Li form a hexagonal lattice,[9] but the ordering within each layer is different from that in C_8Cs and C_8Rb (Fig. 3). The Li atoms may occupy one of three symmetric sets of lattice sites, α, β, or γ. This arrangement is known as the "$\sqrt{3}$ structure". The stacking sequence is simply $\alpha\alpha\alpha \cdots$ (or $\beta\beta\beta \cdots$, or $\gamma\gamma\gamma \cdots$). In analogy with C_8Cs and C_8Rb we expect a transition to a disordered phase at some higher temperature, T_0. Electron diffraction measurements[10] indicate that this transition does indeed take place above room temperature.

The wave vectors of the Li structure are $\vec{q}_1 = (\frac{1}{2}a^*, a^*/2\sqrt{3}, 0)$ and $\vec{q}_2 = -\vec{q}_1$ (Fig. 4). The order parameter thus has two components, $\psi_\pm$. It is convenient to introduce real order parameters $\psi_1 = \frac{1}{2}(\psi_+ + \psi_-)$ and $\psi_2 = (1/2i)(\psi_+ - \psi_-)$ describing cosine and sine waves, respectively, with the wave vector $\vec{q}_1$. The three ordered states are given by

$$\begin{aligned} \rho_1(\vec{r}) &= \cos\vec{q}_1 \cdot \vec{r} \ , \\ \rho_2(\vec{r}) &= -\tfrac{1}{2}(\cos\vec{q}_1 \cdot \vec{r} + \sqrt{3}\sin\vec{q}_1 \cdot \vec{r}) \ , \\ \rho_3(\vec{r}) &= -\tfrac{1}{2}(\cos\vec{q}_1 \cdot \vec{r} - \sqrt{3}\sin\vec{q}_1 \cdot \vec{r}) \ . \end{aligned} \tag{8}$$

These densities have the symmetries of the α, β, and γ arrangements, respectively. The free-energy expansion takes the form

$$F = \frac{1}{2} r \sum_i \psi_i^2 + w(\psi_1^3 - 3\psi_1\psi_2^2) + u_4(\psi_1^2 + \psi_2^2)^2 \ , \tag{9}$$

which defines the three-dimensional three-state Potts model. This equivalence was first shown by Alexander[11] for the two-dimensional case. Note that the expansion has a third-order term. Landau theory therefore predicts a first-order transition. There is, however, conflicting theoretical evidence of the critical behavior of this model.[12] Diffraction experiments on LiC_6 may thus serve to test these various theories. It has been shown by Mukamel *et al.*[13] that a certain phase transition in a cubic ferromagnet in a field is

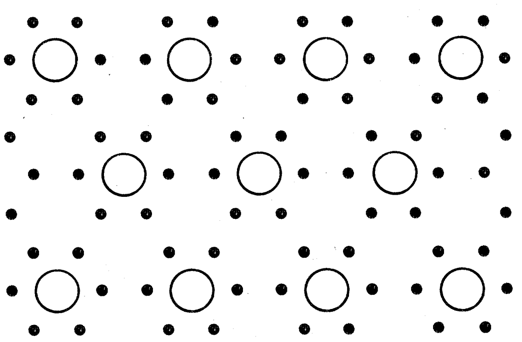

FIG. 3. Intralayer ordering of Li atoms in C_6Li.

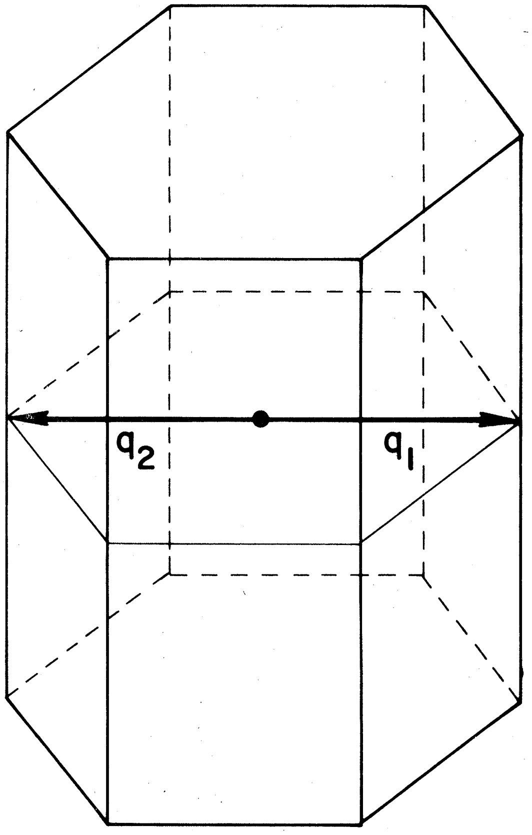

FIG. 4. Wave vectors characterizing the Li ordering in C_6Li.

also described by the three-state Potts model. Experiments[14] on $DyAl_2$ and $SrTiO_3$ show the transition to be first order, but independent experiments are important.

III. SUMMARY AND CONCLUSIONS

We have mapped the melting transitions in C_8Cs, C_8Rb, and C_6Li onto Landau-Ginzburg models, and we found the transitions to be of first order. Similar phase transitions occur in a variety of different intercalation compounds.[4]. In principle, each case has to be analyzed separately, and possibly some of the transitions might be second order. Generally, one can predict that the *high*-stage compounds should all exhibit first-order transitions, since the wave vector is necessarily commensurate in the stacking direction, and the corresponding umklapp term drives the transition order. The possible second-order transitions must be found among systems where the periodicity in the stacking direction is either unaffected or doubled at the transition.

ACKNOWLEDGMENTS

We thank R. Clarke, W. D. Ellenson, and N. Kambe for explaining their experiments to us, and M. Schick for discussions. One of us (E.D.) was supported by the NSF under Grant No. DMR77-12676AO, and by a Dr. Ch. Weizmann fellowship.

---

[1] W. D. Ellenson, D. Semmingsen, D. Guérard, D. G. Onn, and J. E. Fischer, Mater. Sci. Eng. 31, 137 (1977).

[2] R. Clarke, N. Caswell, and S. A. Solin, Phys. Rev. Lett. 42, 61 (1979).

[3] D. Guérard, P. Lagrange, M. El. Makrini, and A. Hérold, Carbon 16, 285 (1978).

[4] G. S. Parry, Mater. Sci. Eng. 31, 99 (1977).

[5] E. Domany, M. Schick, and J. S. Walker, Phys. Rev. Lett. 38, 1148 (1977); E. Domany, M. Schick, J. S. Walker, and R. B. Griffiths, Phys. Rev. B 18, 2209 (1978).

[6] R. B. Potts, Proc. Camb. Philos. Soc. 48, 106 (1952).

[7] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1969), Chap. XIII.

[8] A. G. Khachaturyan [Prog. Mater. Sci. 22, 1 (1978); and references therein] has studied order-disorder transitions in several substitutional and interstitial solid solutions using Landau theory.

[9] D. Guérard and A. Hérold, Carbon 13, 337 (1975).

[10] N. Kambe, M. S. Dresselhaus, G. Dresselhaus, S. Basu, A. R. McGhie, and J. E. Fischer (unpublished).

[11] S. Alexander, Phys. Lett. A 54, 353 (1975).

[12] R. V. Ditzian and J. Oitmaa, J. Phys. A 7, L61 (1974); J. P. Straley, J. Phys. A 7, 2173 (1974); G. Golner, Phys. Rev. B 8, 3419 (1973); J. Rudnick, J. Phys. A 8, 1125 (1975).

[13] D. Mukamel, M. E. Fisher, and E. Domany, Phys. Rev. Lett. 37, 565 (1976).

[14] B. Barbara, M. F. Rossignol, and P. Bak, J. Phys. C 11, L183 (1978); A. Aharony, K. A. Müller, and W. Berlinger, Phys. Rev. Lett. 38, 33 (1977).