Three-Dimensional Continuous Melting in Graphite Intercalation Compounds

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It is shown that three-dimensional continuous melting is possible in the graphite intercalation compounds C_6Eu, C_6Yb, and C_6Ba. The critical behavior is that of the three-dimensional XY model. Diffraction experiments are suggested.

Usually, continuous melting is not possible in three dimensions. There is always a latent heat associated with the melting transition. Within the Landau theory this is because the expansion of the free energy in terms of the appropriate order parameter contains third-order terms.[1] Without exception, this prediction of the Landau theory seems to be correct.[2] In this Letter it is shown that the melting of the rare-earth lattices in the graphite intercalation compounds C_6Eu and C_6Yb may be *continuous* (second order). No third-order terms are allowed in the Landau expansion! This might constitute a unique possibility of studying three-dimensional continuous melting. Experiments should be performed to check this possibility and to measure the associated critical behavior which is predicted to be of the three-dimensional (3D) XY type.

Structurally, the stage-1 intercalation compounds consist of hexagonal graphite layers, with stacking sequence $AAAA\ldots$, between which there are layers of metal ions. Neutron,[3] x-ray,[4] and electron[5] diffraction experiments on C_8Cs, C_8Rb, and C_6Li have revealed phase transitions with some interesting properties. In the high-temperature phase there is no long-range order in the metal system—the metal ions form a liquid within the graphite lattice. At a temperature T_c there is a transition to a "frozen" phase where the alkali ions form a regular three-dimensional crystal. In a diffraction experiment this shows up as a new set of Bragg peaks or "satellites" corresponding to the reciprocal-lattice vectors of the crystal. In a recent paper[6] Bak and Domany analyzed the transitions in these alkali intercalation compounds. We found (somewhat disappointingly) that all the transitions should be discontinuous as usual, despite the fact that third-order terms are not always present. However, the ordering of the metal atoms in the systems to be studied here, C_6Eu, C_6Yb, and C_6Ba, is slightly different. The structure of the Landau expansion is fundamentally changed, and a continuous transition of 3D XY nature may take place.

El Makrini *et al.* have prepared and analyzed the stage-1 rare-earth intercalation compounds C_6Eu and C_6Yb.[7] X-ray diffraction experiments show that in the frozen low-temperature phase the rare-earth ions form triangular lattices within each layer. The space group of the ordered phase is $P6_3/mmc$. One of three symmetric sets of lattice sites, α, β, or γ, is occupied (Fig. 1). This arrangement is known as the "$\sqrt{3}$ structure." The stacking sequence is $\alpha\beta\alpha\beta\ldots$. The rare-earth ions thus form an hcp crystal within the graphite lattice. The Ba ions in C_6Ba exhibit a similar ordering. The order is slightly different from that in C_6Li where the sequence is $\alpha\alpha\alpha\ldots$.[8] At some temperature we expect a transition to a liquid phase, in analogy with the situation for the alkali compounds.

According to the theory of Landau and Lifshitz[9] the phase transition is described by an n-dimensional order parameter transforming as the basis of an irreducible representation of the high-temperature symmetry group, which here is the space group of the graphite crystal. The representations are labeled by the wave vectors giving the periodicity of the ordered phase. The wave vectors characterizing the freezing of the rare-earth lattice are simply the basis vectors of the rare-earth reciprocal lattice. In terms of graphite reciprocal-lattice vectors a^* and c^*, there are two independent ordering wave

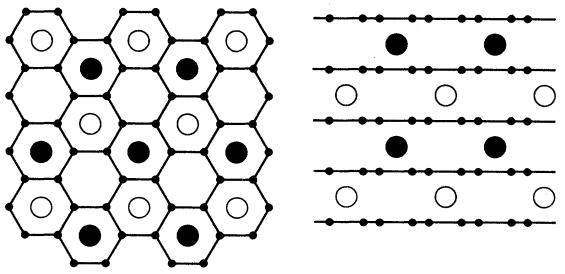

FIG. 1. Intralayer ordering and stacking arrangement of rare-earth or Ba ions in C_6Eu, C_6Yb, or C_6Ba. Open circles, metal atom, $z = 0 + 2n$; filled circles, metal atom, $z = 1 + 2n$; and dots, carbon atom.

vectors (Fig. 2)

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

and

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

The wave vectors which can be formed by applying the graphite point-group symmetries to $\vec{k}_1$ or $\vec{k}_2$ are connected with $\vec{k}_1$ or $\vec{k}_2$ through graphite reciprocal-lattice vectors and they are therefore equivalent to $\vec{k}_1$ or $\vec{k}_2$. The order parameter thus has two components ψ_1 and ψ_2 describing "mass density waves"

$$\rho_i(\vec{r}) = \psi_i \exp(i\vec{k}_i \cdot \vec{r}). \quad (1)$$

It is convenient to introduce real order parameters $\eta_1 = \frac{1}{2}(\psi_1 + \psi_2)$ and $\eta_2 = -\frac{1}{2}i(\psi_1 - \psi_2)$ describing cosine and sine waves, respectively. To verify that the observed $\alpha\beta\alpha\beta\ldots$ structure can indeed be formed by superposition of such waves (and higher harmonics), consider the density function

$$\rho(\vec{r}) = \tfrac{3}{4}\cos(\vec{k}_1' \cdot \vec{r})[(\cos \pi z) + \tfrac{1}{3}] + \tfrac{1}{4}\sqrt{3}\ \sin(\vec{k}_1' \cdot \vec{r})[(\cos \pi z) - 1], \quad (2)$$

where $\vec{k}_1'$ is the projection of $\vec{k}_1$ on the basal plane. For $z = 0$ and 1 the densities within the layers are given by

$$\rho(\vec{r}) = \cos(\vec{k}_1' \cdot \vec{r})$$

and

$$\rho(\vec{r}) = -\tfrac{1}{2}\cos(\vec{k}_1' \cdot \vec{r}) - \tfrac{1}{2}\sqrt{3}\ \sin(\vec{k}_1' \cdot \vec{r}),$$

respectively, which have the symmetries of the α and β arrangements,[6] and so $\rho(\vec{r})$ represents

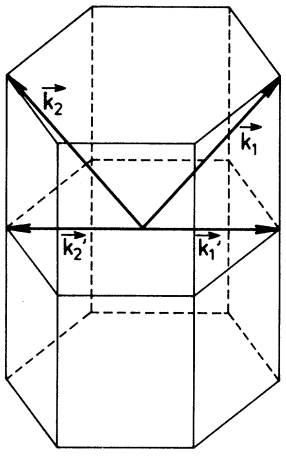

FIG. 2. Brillouin zone of the graphite lattice with the wave vectors characterizing the ordering of the metal ions in C_6Eu, C_6Yb, and C_6Ba.

the $\alpha\beta\alpha\beta$ stacking sequence along the z direction. The maxima of Eq. (2) represent the positions of the metal ions. It is trivial to rewrite (2) as

$$\rho(\vec{r}) = \tfrac{3}{4}\cos(\vec{k}_1 \cdot \vec{r}) + \tfrac{1}{4}\sqrt{3}\ \sin(\vec{k}_1 \cdot \vec{r}) + \tfrac{1}{4}\cos(\vec{k}_1' \cdot \vec{r}) - \tfrac{1}{4}\sqrt{3}\ \sin(\vec{k}_1' \cdot \vec{r}). \quad (3)$$

The first two terms are a superposition of the order parameters, $\eta_1 = \frac{3}{4}$, $\eta_2 = \frac{1}{4}\sqrt{3}$. The last two terms are a superposition of two functions transforming as another $n = 2$ representation labeled by $\vec{k}_1'$ and $\vec{k}_2' = -\vec{k}_1'$. We are thus led to introduce the parameters η_1' and η_2' corresponding to cosine and sine waves with wave vector $\vec{k}_1'$. We shall see that η_1' and η_2' couple to second order in the primary order parameters, and they do not change our main conclusions.

The Landau expansion of the free energy now takes the form

$$F = \tfrac{1}{2}r\textstyle\sum_i \eta_i^2 + u_4(\eta_1^2 + \eta_2^2)^2 + u_6(\eta_1^2 + \eta_2^2)^3 + u_6'(\eta_1^6 - 15\eta_1^4\eta_2^2 + 15\eta_1^2\eta_2^4 - \eta_2^6). \quad (4)$$

This defines the 3D XY model with sixfold anisotropy given by the u_6' term. Note that there are *no third-order terms* in contrast to the situation for the usual isotropic melting. The reason is that it is not possible to form a graphite reciprocal-lattice vector by adding an odd number of $\vec{k}_1$ or $\vec{k}_2$ vectors because of the $\frac{1}{2}c^*$ component. *A second-order transition is therefore allowed.* None of Landau's rules are violated. The critical behavior is that of the 3D XY model. For example, the exponent β is ~ 0.33.[10] The intensities of the Bragg satellites at $\vec{k}_1$ or $\vec{k}_2$ positions are thus given by

$$I \sim (T_c - T)^{2\beta} \sim (T_c - T)^{0.66} \quad (5)$$

near the critical temperature. The sixth-order anisotropy is generally believed to be irrelevant with respect to the critical behavior.[10]

The secondary-order parameter (η_1', η_2') is induced by additional terms in the expansion

$$F' = r'\textstyle\sum_i \eta_i'^2 + v(\eta_1'^3 - 3\eta_1'\eta_2'^2) + w[(\eta_1^2 - \eta_2^2)\eta_1' - 2\eta_1\eta_2\eta_2']. \quad (6)$$

The w term couples the order parameters. For $r' > r$, $u_6 < 0$, $v > 0$, and $w < 0$ the free energy given by (4) and (6) is minimized by the linear combinations of the order parameters characterizing the $\alpha\beta\alpha\beta\ldots$ structure. The equivalent stacking ar-

rangements are given by

$$\begin{aligned}
&\alpha\beta\alpha\beta\text{: } \eta_1=\tfrac{3}{4},\ \eta_2=\tfrac{1}{4}\sqrt{3},\ \eta_1'=\tfrac{1}{4},\ \eta_2'=-\tfrac{1}{4}\sqrt{3};\\
&\beta\alpha\beta\alpha\text{: } \eta_1=-\tfrac{3}{4},\ \eta_2=-\tfrac{1}{4}\sqrt{3},\ \eta_1'=\tfrac{1}{4},\ \eta_2'=-\tfrac{1}{4}\sqrt{3};\\
&\alpha\gamma\alpha\gamma\text{: } \eta_1=\tfrac{3}{4},\ \eta_2=-\tfrac{1}{4}\sqrt{3},\ \eta_1'=\tfrac{1}{4},\ \eta_2'=\tfrac{1}{4}\sqrt{3};\\
&\gamma\alpha\gamma\alpha\text{: } \eta_1=-\tfrac{3}{4},\ \eta_2=\tfrac{1}{4}\sqrt{3},\ \eta_1'=\tfrac{1}{4},\ \eta_2'=\tfrac{1}{4}\sqrt{3};\\
&\beta\gamma\beta\gamma\text{: } \eta_1=0,\ \eta_2=-\tfrac{1}{2}\sqrt{3},\ \eta_1'=-\tfrac{1}{2},\ \eta_2'=0;\\
&\gamma\beta\gamma\beta\text{: } \eta_1=0,\ \eta_2=\tfrac{1}{2}\sqrt{3},\ \eta_1'=-\tfrac{1}{2},\ \eta_2'=0.
\end{aligned} \tag{7}$$

These combinations all minimize the free energy. The intensities I' of the secondary peaks at $\vec{k}_1'$ and $\vec{k}_2'$ are a measure of η_1' and η_2'. The numbers in the equation give the relative values of η_1 and η_2, and of η_1' and η_2'. The relative size of the two secondary and the two primary order parameters depends on the parameters in (6), and on the temperature. The temperature dependence of the coupled order parameters η_1' and η_2' is described by an exponent

$$\beta' = 2 - \alpha - \varphi, \tag{8}$$

where φ is an appropriate crossover exponent.[11] An ϵ-expansion analysis ($\epsilon = 4-d$) yields

$$\beta' = 1 - \frac{2\epsilon}{10} + \frac{6\epsilon^2}{100} \quad (=0.86 \text{ for } d=3), \tag{9}$$

and so

$$I' \sim (T_c - T)^{2\beta'} \sim (T_c - T)^{1.72} \tag{10}$$

near T_c. Above T_c the correlations between planes are usually much shorter than within planes. However, long-range order probably always sets in simultaneously between planes and within planes as has been assumed in this paper. Also, it should be mentioned that stoichiometry is not a necessary condition for the second-order transition. There is no unique relation between the wave vector of the "mass density wave" and the chemical composition since the ρ's are probability distribution functions.[6]

In conclusion, I have shown that the melting transitions of the rare-earth or barium sublattices in C_6Yb, C_6Eu, and C_6Ba are allowed to be continuous, and I have determined the critical behavior. Diffraction experiments should be performed to check the predictions.

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[1]See S. Alexander and J. P. McTague, Phys. Rev. Lett. 41, 702 (1978), and references therein.

[2]For $d=2$, B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. 41, 121 (1978), have constructed a theory which allows a continuous transition.

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

[4]R. Clarke, N. Caswell, and S. A. Solin, Phys. Rev. Lett. 42, 161 (1979).

[5]N. Kambe, M. S. Dresselhaus, G. Dresselhaus, S. Basu, A. R. McGhie, and J. E. Fischer, Mater. Sci. Eng. 40, 1 (1979). These authors find the stacking sequence $\alpha\beta\gamma$ for C_6Li at low temperatures and several possible stacking arrangements at higher temperatures.

[6]P. Bak and E. Domany, Phys. Rev. B 20, 2818 (1979). For an illuminating discussion on the Landau theory, see E. Domany, M. Schick, J. S. Walker, and R. B. Griffiths, Phys. Rev. B 18, 2209 (1978).

[7]M. El Makrini, D. Guérard, P. Lagrange, and A. Hérold, to be published, and private communications.

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

[9]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1964), Chap. 13.

[10]M. E. Fisher, Rev. Mod. Phys. 46, 597 (1974).

[11]R. A. Cowley and A. D. Bruce, J. Phys. C 11, 3577 (1978).