Phase transitions in some intercalation graphite compounds

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A model describing the structural properties of metal atom penetration into graphite (the case of strong intercalation) is proposed. Phase transitions between ordered phases are examined. The theoretical analysis is compared with experimental data.

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Among a large class of intercalated substances, compounds based on graphite are characterized by a high degree of intra- and interlayer ordering. This paper concerns the structural properties of graphite strongly intercalated with alkali atoms. These compounds include C_8K, C_8Cs, C_8Rb, and C_6Li. In these compounds, a layer of metal atoms is situated between two successive carbon layers. In addition, the hexagonal planes of carbon form an *AAA* ... type spatial packing, i.e., these layers are situated exactly above each other. The atoms of the implanted metal are situated above the centers of the hexagons in the graphite layer, and their ordered state in the plane is shown in Figs. 1 and 2. It is evident from the figures that there are four equivalent positions (α, β, γ, and δ) of the sublattice of alkali atoms for compounds of the type C_8K and three for C_6Li. It is known experimentally[1-3] that a $\alpha\beta\gamma\delta$ sequence of rubidium layers forms in C_8Rb at room temperature. The same kind of joining is characteristic of the low-temperature phase of C_8K. A different sequence of the type $\alpha\beta\gamma$ is found in C_8Cs. The high-temperature phase of C_8Rb ($T \sim 700$ K) corresponds to $\alpha\beta$ ordering. Here we shall discuss the possible types of spatial packing of metal layers, as well as phase transitions between them.

The planar structure of metal atoms, shown in Fig. 1, is described by the four-component Potts model.[4,5] There are basically two mechanisms for the interlayer interaction. These are an electrostatic interaction[6] as well as an elastic interaction.[7] The latter is related to the fact that metal atoms in a graphic sandwich create a force couple with zero

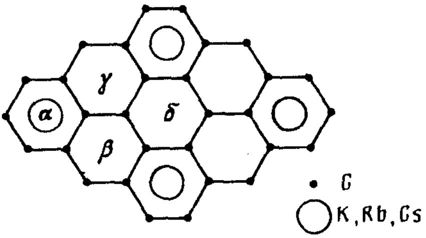

FIG. 1.

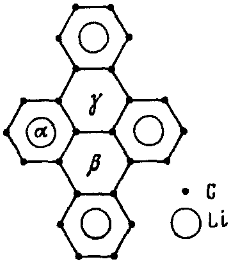

FIG. 2.

moment, oriented along the normal to the layers. The interaction of alkali atoms, forming regular planar structures, is quite appreciable at distances that do not greatly exceed the dimension of their unit cell. At large distances, the interaction decreases exponentially. It is significant that the interlayer interaction depends only on whether or not the metal layers occupy identical positions, and for this reason it is described by the same type of Potts model. Thus, the energy of a type $\alpha\alpha$ interaction differs from $\alpha\beta$, but the latter is the same for $\alpha\gamma$, $\beta\delta$, and so on.

It is convenient to represent the Hamiltonian, describing the system of alkali atoms, in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1\,, \; \mathcal{H}_0 = -\sum_{j,\mathbf{r},\mathbf{r}'} I_0(\mathbf{r} - \mathbf{r}')\,\Delta(a_j(\mathbf{r}),\, a_j(\mathbf{r}'))\,, \tag{1}$$

$$\mathcal{H}_1 = \frac{1}{2}\sum_{l \neq 0, j, \mathbf{r}} I_l\,\Delta(a_j(\mathbf{r}),\, a_{j+l}(\mathbf{r}))\,,$$

where j enumerates the layers, $\mathbf{r}$ is the coordinate of a site in a planar sublattice of metal atoms. The first term represents the intralayer attraction, while the second term describes the interlayer repulsion. We shall also assume that there is an anisotropy owing to the layered structure of graphite: $I_0 \gg I_1, I_2 \ldots$. The variable Δ entering in the Hamiltonian (1) is related to the traceless order parameter in the four-component Potts model:

$$\Delta(a_j(\mathbf{r}),\, \mu) = \delta(a_j(\mathbf{r}),\, \mu) - {}^1\!/_4 \;. \tag{2}$$

Here $\alpha_j(\mathbf{r})$ can assume one of four values: α, β, γ, or δ. The order parameter satisfies the following relation:

$$\Delta(a,\; \beta) = \sum_{\mu} \Delta(a, \mu)\; \Delta(\beta, \mu). \tag{3}$$

It was shown in Ref. 8 for the anisotropic Ising model that the best method in models of this kind is a high-temperature expansion with respect to the interlayer interaction. In this case, the spatial ordering turns out to be a function of layer characteristics such as the spontaneous ordering in a layer, the irreducible two-dimensional susceptibility, and so on. This method turns out to be valid not only at high T, but over the entire temperature scale with the exception of a narrow region near the transition temperature for a separate layer. The actual expansion parameter will be presented below.

The free energy can be represented as a series in irreducible averages (they are denoted by the brackets $\langle \ldots \rangle$):

$$F = F_0 + \sum_{n=1}^{\infty} (-1)^{n-1} < \mathcal{H}_1^n > /\, T^{n-1} n! \tag{4}$$

The first order of this expansion corresponds to the self-consistent-field approximation in the Hamiltonian $\mathcal{H}_1$. The order parameter is averaged independently in each plane:

$$\overline{\Delta(a_j(\mathbf{r}),\, \mu)} = \Delta_0(T)\; (\delta(a_j,\, \mu) - {}^1\!/4). \tag{5}$$

The contribution of the interlayer interaction to the free energy, using (3)-(5), can be written as follows:

$$F_1 = N_p \sum_{l \neq 0, j} I_l \, \Delta_0^2 \left(\delta (a_j , a_{j+l}) - 1/4 \right), \tag{6}$$

where N_p is the number of sites in the planar sublattice of metal atoms.

Let I_l be repulsive ($I_l > 0$). In the zeroth approximation, all layers are independent and, although the order parameters in them differ from zero, their sequence is random. Taking into account the nearest coupling I_1 leads to partial removal of degeneracy: configurations of the type $\alpha\alpha$ become forbidden. The interaction I_2 forbids sequences of the type $\alpha\beta\alpha$ and others. Only I_3 removes degeneracy: giving the first triplet, for example $\alpha\beta\gamma$, uniquely determines the entire sequence $\alpha\beta\gamma\alpha\beta\gamma\alpha\ldots$ for $I_3 < 0$ and $\alpha\beta\gamma\delta\alpha\beta\gamma\delta\alpha\ldots$ for $I_3 > 0$.

The next orders of the high-temperature expansion of the free energy involve taking into account the thermal-fluctuation interaction between layers.[8] We shall introduce a quantity analogous to the irreducible susceptibility in the Ising model:

$$\chi(T) = \frac{1}{3T} \sum_{\mathbf{r}} < \Delta(a_j \ (0), a_j \ (\mathbf{r}) \ ) >. \tag{7}$$

Our analysis is valid when the condition $\chi I_1 \ll 1$ is satisfied. The temperature dependence of χ is the same as that in the Ising model, very slow at low temperatures $\sim \exp \times (-\mathrm{const}/T)$, and varying rapidly near the temperature of the two-dimensional phase transition. The effective interaction constants I_2 and I_3 turn out to depend on the temperature as follows:

$$I_2(T) = I_2 - \chi I_1^2 , \tag{8}$$

$$I_3(T) = I_3 - 2\chi I_1 I_2 + \chi^2 I_1^3 . \tag{9}$$

Assuming that $I_1 \gg I_2 \gg I_3$, we can distinguish the possibilities illustrated in Fig. 3. This figure shows the phase diagram of the model examined and present "trajectories" of the effective constants (8)-(9). One pair of initial values I_2 and I_3 corresponds to a sequence of phase transitions of the type $\alpha\beta\gamma\delta \to \alpha\beta\gamma \to \alpha\beta$, while another corresponds to the sequence $\alpha\beta\gamma\delta \to \alpha\beta$. The latter case corresponds to the inequality $I_3 \gtrsim I_2^2 / I_1$. This simple mechanism explains phase transitions between ordered configurations of layers that are observed in strongly intercalated graphite compounds.

In conclusion, we should make several remarks. In C_8Rb and C_8K, phase transitions occur according to the scheme $\alpha\beta\gamma\delta \to ? \to \alpha\beta$. The intermediate region here has not been adequately studied. The question as to whether or not an intermediate phase $\alpha\beta\gamma$ exists in these substances remains open.

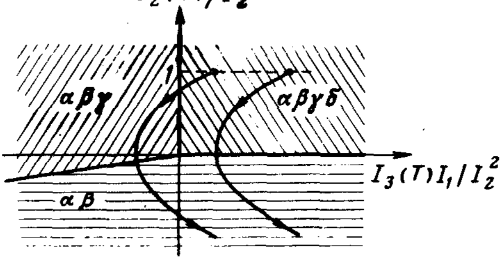

FIG. 3.

Such a joining ($\alpha\beta\gamma$) occurs in C_8Cs in the low-temperature phase. This must indicate that in this substance the direct interaction constant I_3 is small and the fluctuation interaction exceeds it. In this compound, the transition $\alpha\beta\gamma \rightarrow \alpha\beta$ should be expected with increasing temperature.

We should also expect that near transitions of the type $\alpha\beta\gamma\delta \rightarrow \alpha\beta\gamma$ and $\alpha\beta\gamma \rightarrow \alpha\beta$ the line of phase confluence splits with the formation of cells with a larger spacing, for example, $\alpha\beta\gamma\delta\alpha\beta\gamma$ or $\alpha\beta\gamma\alpha\beta$. The region of existence of these phases, however, is small with respect to the parameter χI_1. We should note the fact that the phase transitions examined here are first-order transitions and are accompanied by hysteresis phenomena and macroscopic mass transfer, which complicates their observation.

We shall make one final remark. The existence of phases of the type $\alpha\alpha\alpha$ was observed experimentally in the compound C_6Li. Evidently, the chemical bond between lithium and carbon leads to attraction ($I_1 < 0$) between the neighboring layers.

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