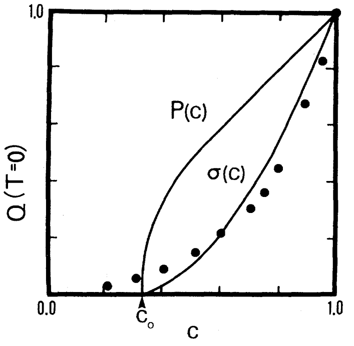

FIG. 2. Zero-temperature order parameter as a function of quadrupole concentration. The solid curves show percolation probability $P(c)$ and conductivity $\sigma(c)$ for the infinite simple-cubic lattice, as given in Ref. 7. c_0 is the percolation threshold.

namic response of the quadrupolar system and to understand the form of the excitation spectrum present in this sort of glasslike ordering. This is obviously a nontrivial undertaking, and to my knowledge, remains to be done.

My results lead me to believe that a quadrupolar interaction can cause local metastable ordering in certain crystal structures. This ordering is characterized by a rotational freezing, with some proportion of the molecules locked into a locally defined orientation. It seems to be accompanied as well by the sort of susceptibility cusp typical of the usual spin-glass susceptibility. My results with respect to energy and specific heat are somewhat more ambiguous and suggest no strong specific-heat anomaly at the transition. As the quadrupole concentration is lowered, the ordering is destroyed in a manner reminiscent of the reduction of the analogous network conductivity, at least for the particular lattice studied. Work currently in progress includes study of the behavior of the temperature-dependent properties of such systems as they are diluted, and of their dynamic response functions.

I am grateful to D. G. Haase for long and patient explanations of the experimental aspects of the problem.

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Phase Transitions in Potassium-Intercalated Graphite: KC_{24}

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Two structural phase transition in KC_{24} have been observed by x-ray diffraction: an order-disorder transition at $T_U = 126.0 \pm 0.5$ K and a structural transition T_L at about 93 K. Details of these transitions are presented, as well as the stacking sequences of the intermediate and low-temperature phases.

The existence of graphite intercalation compounds in which metal-atom layers are inserted between graphite layers has been known for almost fifty years. These systems have been of interest recently because of the high basal-plane conductivity and the highly two-dimensional nature of the electronic structure in some of these compounds.[1] X-ray structural studies on stage-2 alkali-metal compounds[2] MC_{24} (M = K, Rb, Cs) have shown the existence of an order-disorder transition. However, recent resistivity measurements[3] have shown not one but two anomalies as a function of temperature for each compound. For the three metals, one of each pair of transitions can be correlated with the single order-disorder transition temperature reported earlier.[2]

In this Letter we report x-ray scattering results which reveal the structural nature of the two low-temperature phase transitions in KC_{24}, a stage-2 graphite intercalation compound. The upper transition, $T_U = 126.0 \pm 0.5$ K, is an order-disorder transition involving the potassium intercalant while the lower transition T_L, at about 93 K, is a structural transition involving a change in the c-axis stacking of intercalant layers. The unusual scattering profiles observed in the intermediate phase are reproduced (within experimental error) by a model with stacking faults in the graphite and intercalant layers.

The x-ray scattering data were collected on a three-axis x-ray spectrometer using Cu $K\alpha$ radiation from a sealed tube. A pyrolytic graphite monochromator and pyrolytic graphite analyzer were used to reduce background. The sample, made from highly oriented pyrolytic graphite,[4] in the usual way,[5] had dimensions $0.5 \times 1 \times 0.01$ cm^3 and was sealed in glass throughout the measurement. The sample has a well-defined c direction but random orientation of the in-plane a and b directions. For all measurements, the graphite c axis was in the scattering plane. This geometry allows both the in-plane structure as well as the stacking sequence to be studied.

Scans were performed from room temperature down to approximately 10 K. At high temperatures, two different contributions to the scattering were observed: that from the ordered carbon-layer networks and that from the disordered potassium intercalant. The latter appeared as relatively broad peaks of in-plane scattering (no variation of the l component). The strongest peak was centered at about 1.20 Å^{-1}, which reflects the expected average in-plane distance for disordered intercalant species in this compound of composition KC_{24}. Intensity was also observed about 2.40 Å^{-1}.

Below T_U, in the intermediate phase, diffraction peaks arising from the ordering of the potassium intercalant were observed. The positions, in reciprocal space, of the more intense peaks are shown schematically in Fig. 1. As in previous studies,[2] the sample appears to have ordered into a number of structures, giving rise to a multitude of diffraction peaks. Interestingly, cycling of the temperature always led to essentially the same diffraction pattern with only small changes in relative intensities. If the potassium lattice only ordered in the plane at T_U, it would have given rise to uninterrupted cylinders of scattering parallel to l. This was not ob-

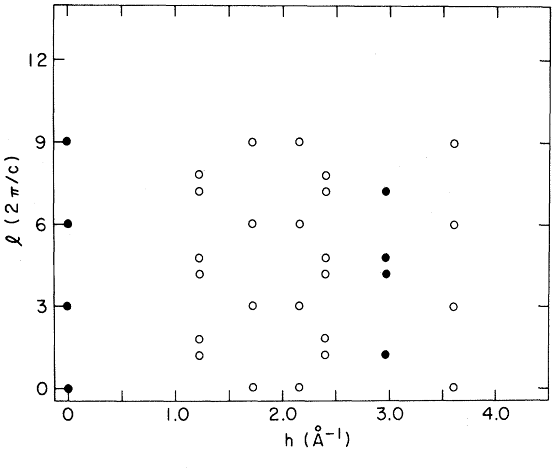

FIG. 1. Schematic representation of the reciprocal space for the more intense Bragg peaks of the intermediate phase at $T = 120$ K. c is 26.5 Å, the repeat distance in the c direction of this phase, equal to 3 carbon-metal-carbon sandwich thicknesses. The open circles are scattering from the intercalant. The closed circles are scattering both from the graphite and intercalant.

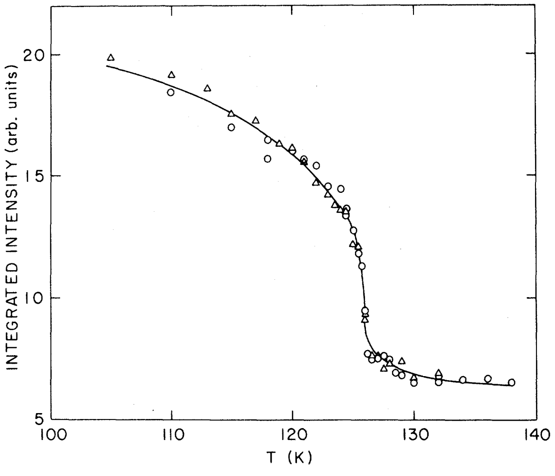

FIG. 2. Temperature dependence of the integrated intensity of the 1.71-Å^{-1} powder peak, with $l = 0$. Triangles are heating, circles cooling. The solid line is a guide to the eye.

served, as is indicated in Fig. 1. At T_U both in-plane and c-axis stacking occur.

The order parameter of the upper transition was measured by observing the temperature dependence of one of the peaks arising from potassium ordering, the 1.71-Å^{-1} peak. These data are shown in Fig. 2 and indicate a higher-order phase transition. The widths of the diffraction profiles narrow to resolution-limited peaks as T_U is approached from above, indicating that the tail, seen in Fig. 2, is critical scattering. Below T_U, the intensity increases rapidly and smoothly to a saturated value as in a second-order transition.

Two very interesting features of the intermediate phase are (1) the 1.71 Å^{-1} and also other peaks arising from the ordered intercalant are not exactly commensurate with the carbon-layer substrate as calculated from the (110) ($h = 5.084$ Å^{-1}) and (101) ($h = 2.935$ Å^{-1}) peaks of the graphite matrix and (2) several series of peaks in the l direction, in particular the $(10l)$ graphite peaks and also many from the intercalent do not appear at integral values of l and are broadened, as shown in Fig. 3.

We have found that the displacement and broadening of the peaks can be understood in terms of stacking faults. The features of the $(10l)$ ($h = 2.935$ Å^{-1}) peaks arising from the graphite matrix are present at room temperature and do not change down to approximately 10 K. The previous work[2] showed the ideal stacking sequence below the order-disorder transition for the Cs and Rb compounds to be $A\alpha AB\beta BC\gamma CA\ldots$, where the graphite stacking is indicated by the Roman letters and the metal by the Greek letters. This is also found in the present measurements of the potassium compound in the intermediate phase. The metal layers prefer to be surrounded by like graphite neighbors (as in the $A\alpha A$ sequence). The possibility of stacking faults is quite likely in this system since there has to be significant motion of the carbon layers from the $ABAB\ldots$ stacking of pure graphite to arrive at the stage-2 stacking sequence indicated above.

We have calculated the scattering profiles for a model of the graphite intercalation compound made of sandwiches of like graphite layers with a metal layer in the middle. In this model an unfaulted region would have $ABCABC\ldots$ stacking of sandwiches as in the fcc structure, and the features in the diffraction profiles observed for KC_{24} are the same as those found in fcc metals with stacking faults. This calculation makes use of a simple, exact method[6] for obtaining the appropriate correlation functions in a one-dimensionally disordered system. Next-nearest-neighbor interactions, required to give the above stacking sequence, were included. A single parameter, α, the probability of finding a fault going from one sandwich to another, is adjusted to give agreement with experiment. The results, with $\alpha = 0.38$, are shown in Fig. 3 for both graphite and potassium peaks. Each profile shows two peaks that would occur at integral values of l in the unfaulted structure. This value of α corresponds to an average unfaulted region of about 2.5 carbon-metal-carbon sandwiches, less than one complete stacking repeat distance. Thus in the intermediate phase the potassium-graphite interaction is strong enough that the ordered potassium structure exhibits the same faulted structure as does the graphite matrix.

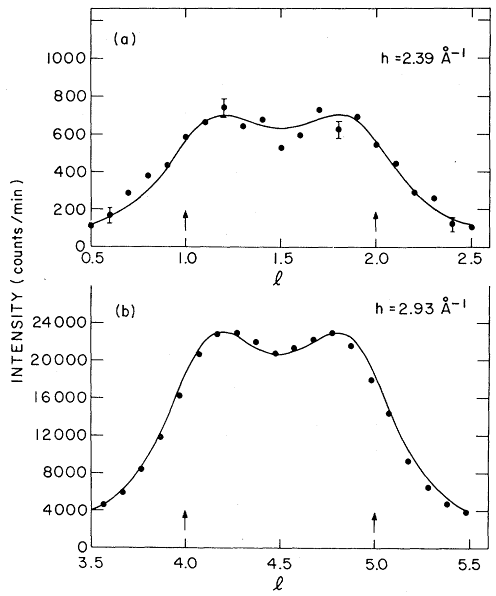

FIG. 3. (a) Scan along l of two powder peaks from the intercalant at $T = 120$ K, in the intermediate phase. The solid circles are the measured data and the solid line the calculation with the stacking-fault parameter $\alpha = 0.38$. Arrows indicate the peak positions in an unfaulted structure. (b) Scan along l of two $(10l)$ graphite peaks also at $T = 120$ K. Again the solid circles are the measured points and the line a calculation with $\alpha = 0.38$. Arrows indicate the peak positions in an unfaulted structure.

The lower transition is not nearly as well defined as the upper, since the sample has ordered in more than one structure. However, between 95 and 90 K the sample undergoes a solid-solid phase transition which appears to be first order.

The scattering in the low-temperature phase is shown schematically in Fig. 4. In the transition from the intermediate to the low-temperature phase, some of the potassium diffraction peaks shift in the plane. In particular the 1.71-Å^{-1} potassium peak shifts to the commensurate position of 1.69 Å^{-1}, calculated from the ($10l$) and (110) peaks from the graphite matrix. Also in this phase, the stacking is the same as that observed by Parry and co-workers[2]: $A\alpha AB\beta BC\gamma CA\alpha' AB\beta' BC\gamma' CA\ldots$. In this sequence the metal-metal interaction must extend at least to 26 Å, the α-α' separation. This stacking manifests itself in the diffraction pattern by peaks appearing at half-integral values of l ($l = 2\pi/c$, $c = 26.5$ Å, the thickness of three carbon-metal-carbon sandwiches). This yields the quite large unit cell of six metal sandwich units. In addition the intercalant peaks have narrowed, indicating the absence of stacking faults in the potassium lattice in this phase, while the underlying graphite layers do not change their stacking.

Neither of the phase transitions observed here has a large effect on the electronic properties.[3] Unlike other layered systems, the conductivity remains metallic at all temperatures and the resistivity anomalies are only of the order of 5% at T_U and T_L. The magnetic susceptibility is continuous through both phase transitions.[7] The occurrence of two resistivity anomalies in donor compounds is consistent with many observations[8] that the electronic structure is not highly anisotropic; because of this small anisotropy, the carrier scattering is sensitive to both kinds of disorder. In the high-temperature region ($T > T_U$) excess carrier scattering arises from the two-dimensional disorder of the intercalant layers; in the intermediate phase ($T_U < T < T_L$) excess scattering arises from the c-axis stacking faults. In contrast, $\rho(T)$ in acceptor compounds generally exhibits only one anomaly of much greater amplitude. This can be understood as a manifestation of the highly two-dimensional character of the intercalant electron wave functions so that the two-dimensional disorder of the intercalant is important to the electronic properties while the stacking disorder, if present, plays no role.

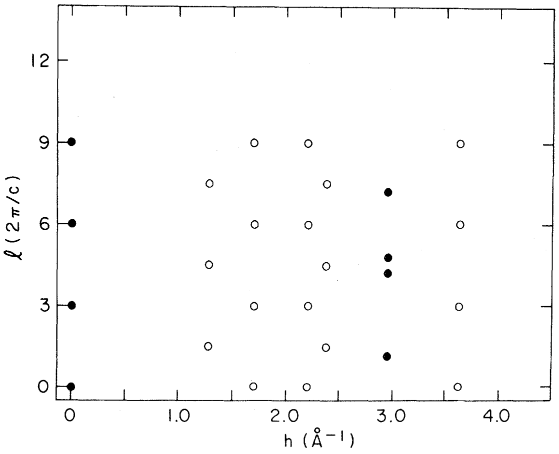

FIG. 4. Schematic representation of the reciprocal space of the more intense Bragg peaks of the low-temperature phase at $T = 80$ K. c is the same as in Fig. 1. The open circles are scattering from the intercalant. The closed circles represent scattering from both the graphite and intercalant.

In summary, we have shown the presence of two transitions in stage-2 potassium-intercalated graphite. The intermediate-phase stacking is the same as that seen in the stage-2 Cs and Rb compounds below their order-disorder transitions.[2] Because of multiple phases in the in-plane structure is extremely difficult to determine; however, the stacking sequences and associated scattering along the l direction have been interpreted with a simple model of faulting. The presence of the stacking faults, and their effect on the potassium ordering and the critical temperature of the upper transition, might be understood in the framework of phase transitions in the presence of a random field. These possibilities are being investigated with a range of sample-preparation conditions.

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Phase Separation and Gelation in Gelatin Gels

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We present evidence for the existence of phase separation in gelatin gels having methanol-water mixtures as the gel fluid. The curves for the liquid-gel transition and the spinodal line were determined using measurements of viscosity and of scattered or transmitted light intensity, respectively. For the 30%-methanol–water mixture, the gelation curve terminates at the critical point. We also analyze the observed phase equilibria of the gels with a simple mean-field theory.

The existence of phase separation in covalently crosslinked gels has recently been established.[1,2] In this Letter, we present evidence that critical phenomena and phase separation also occur in weakly crosslinked gels in which the gel network can undergo the liquid-gel transition reversibly. We report results of light-scattering and viscosity measurements used to determine the spinodal line and the gel-sol transition for gelatin-water-methanol systems. We also present a simple mean-field-theory analysis which describes the results of these measurements. The theory predicts that the temperatures of the two transitions can be varied independently by adjusting the solvent composition and the length of the polymer molecules comprising the network. That two very different transitions are occurring in a single system makes gelatin-water-alcohol an especially interesting system to study in terms of critical phenomena and the bond percolation problem.[3]

Calf-hide gelatin (General Foods Corp.) was dissolved in mixtures of distilled water and methanol with compositions of 0, 10, 30, and 50 volume percent methanol. The weight concentration of gelatin ranged from 0.2% to 60%. According to the manufacturers, the average molecular weight of this gelatin is 10^5 dalton (1 dalton = 1 amu).

The liquid-gel transition temperature was determined by measuring the viscosity of the samples as a function of temperature. We employed the rolling-ball method of viscometry using micropipettes (inner diameter = 1.3 mm) and microballs (diameter = 0.025 mm). Figure 1 shows the results of such a measurement with the inverse of the viscosity plotted versus temperature for a sample made of 7% gelatin and 30% methanol. As the temperature is lowered, the viscosity increases. At 28°C, the viscosity appears to diverge. This temperature is taken to be the liquid-gel transition temperature.

The spinodal line is defined to be the point at which concentration fluctuations in the sample diverge. This point is readily observed, as the sample then becomes opaque. We determined the spinodal temperature for the various samples by measuring either the transmitted light intensity or the intensity of the light scattered at 90° as a function of temperature. Transmission measurements were used when it was necessary to avoid multiple scattering associated with very strong scattering in the intensity measured at a 90° angle. The gel samples were placed in 5-mm-diam culture tubes. Temperature control of the sample holder was achieved to an accuracy of 0.05°C