

Intercalant ordering and lattice dynamics in stage-1  $\text{KHgC}_4$ 

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Neutron scattering methods were used to investigate intercalant ordering and phonon spectra in  $\text{KHgC}_4$  at 297 and 12 K. Two coexisting phases, each three dimensionally ordered, were observed in a bulk sample, with  $2 \times 2$  and  $\sqrt{3} \times 2$  registry of the intercalant superlattices with respect to graphite. The phonon measurements show that out-of-plane Hg vibrations have lower frequencies than in-plane intercalant motions. Accurate measurement of the C-C bond distance indicates a smaller charge transfer to C layers in  $\text{KHgC}_4$  than in  $\text{MC}_8$  ( $M = \text{K}, \text{Rb}, \text{Cs}$ ).

The graphite intercalation compounds  $\text{KHgC}_4$  (stage 1) and  $\text{KHgC}_8$  (stage 2) have recently been found<sup>1,2</sup> to exhibit unusual superconducting properties, especially under high pressure. The crystal structures are not known in detail, and the results presented here are the first firm evidence that the intercalant in  $\text{KHgC}_4$  is three dimensionally ordered. Recent electron diffraction experiments<sup>3</sup> have shown that several in-plane ordering arrangements are possible, with the formation of  $(2 \times 2)R 0^\circ$ ,  $(\sqrt{3} \times 2)R (30^\circ, 0^\circ)$ , and  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  superlattices with respect to adjacent graphite layers. We observe the first two of these structures as distinct phases coexisting in our large sample of  $\text{KHgC}_4$ . In addition, we have measured phonon dispersion curves for out-of-plane vibrations, and a spectrum which reflects the main features of the in-plane phonon density of states for the intercalant.

The sample was prepared by a vapor transport method, starting with an excess amount of a one-to-one mixture of high-purity K and Hg and a  $25 \times 15 \times 1\text{-mm}^3$  slab of Union Carbide grade ZYH pyrolytic graphite, placed at opposite ends of an evacuated glass tube. The KHg was held at  $190^\circ\text{C}$  and the graphite at  $200^\circ\text{C}$  for a three-week reaction period. Elastic and inelastic neutron scattering experiments were performed on a triple-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory, with a fixed scattered-neutron energy of 13.7 meV.

Our elastic scattering measurements reveal the presence of at least two phases coexisting in our sample, as summarized in Fig. 1, which shows the appearance of reciprocal space as observed in the experiment. Because our sample was synthesized from pyrolytic graphite, in which the crystallites comprising the material have a common aligned  $c$  axis, but random orientation in the basal plane, these data are cylindrically averaged about the  $c$  axis. By comparing the most intense  $(00l)$  reflections of each component, their relative amounts were estimated to be approximately 93% for the majority phase, which was found to have an intercalate package thickness (= C-C interplanar distance)  $l_c = 10.24 \text{ \AA}$  at 297 K, and about 7% for the minority phase, with  $l_c = 10.83 \text{ \AA}$ . The intercalant ordering is observed to

be essentially three dimensional for both phases, leading to distinct peaks along scans  $B$  through  $E$  in Fig. 1, rather than diffuse rods of intensity. There is stacking fault smearing present, as discussed below, but clearly the positional correlations from layer to layer are strong.

The intercalant ordering peaks from the majority phase (scans  $B$  and  $E$ , the latter shown in Fig. 2) imply a  $2 \times 2$  triangular in-plane ordering. The spots occur at wave vectors  $(h, l) = (\frac{1}{2}, n + \frac{1}{2})$  and  $(\frac{\sqrt{3}}{2}, n + \frac{1}{2})$ , in units of  $(4\pi/\sqrt{3}a, 2\pi/l_c)$ , where  $a = 2.47 \text{ \AA}$  is the graphite layer lattice parameter. These peaks arise purely from intercalant (K, Hg) scattering. In scan  $F$ , along the first lattice row where

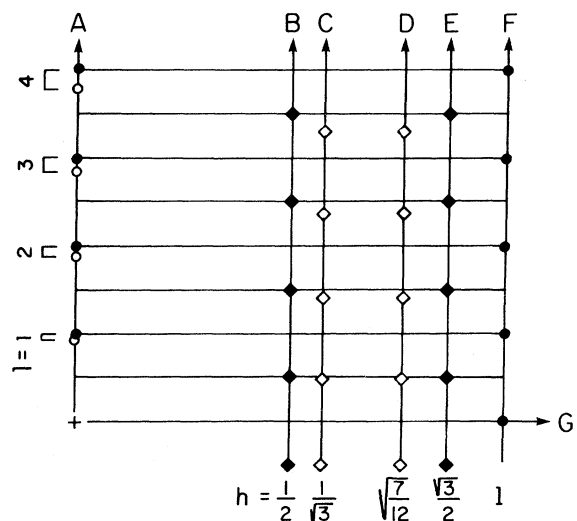


FIG. 1. Cylindrically averaged reciprocal space of  $\text{KHgC}_4$ . Closed and open symbols refer to majority ( $2 \times 2$ ) and minority ( $\sqrt{3} \times 2$ ) phases, respectively. Diamond-shaped spots are due solely to intercalant (KHg) ordering, but all atoms (K, Hg, C) contribute to circular spots. Letters  $A-G$  label the diffractometer scans used in the experiment.

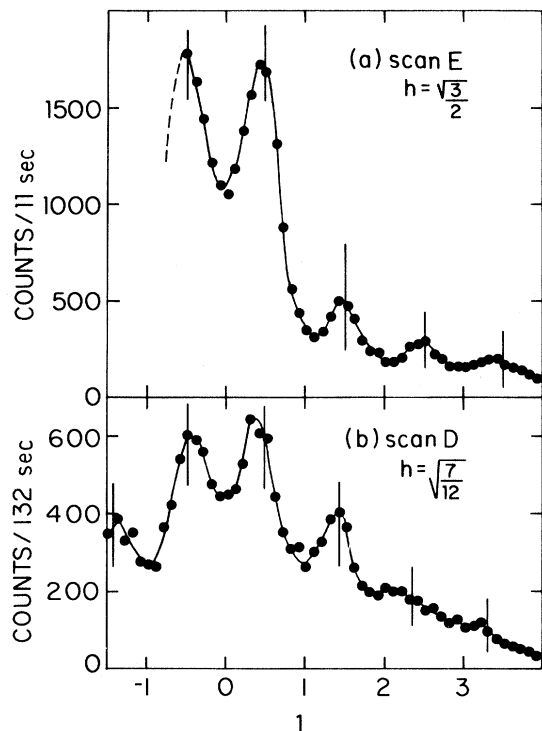


FIG. 2. Intercalant ordering peaks in  $\text{KHgC}_4$ . Short vertical lines show indexing with (a)  $I_c = 10.24 \text{ \AA}$  (majority phase) and (b)  $I_c = 10.83 \text{ \AA}$  (minority phase). The units of  $l$  on the horizontal axis are  $2\pi/10.24 \text{ \AA}^{-1}$ .

graphite scattering is present, a set of somewhat (approximately three times) more intense reflections is observed at positions  $(1, n)$ . Although the latter must contain appreciable contributions from K and Hg scattering, the intensities and peak profiles are dominated by graphite scattering. The  $(1, n)$  reflections are found to be considerably sharper than the  $(\frac{1}{2}, n + \frac{1}{2})$  and  $(\sqrt{3}/2, n + \frac{1}{2})$  reflections, indicating that the graphite stacking sequence is well-ordered along  $c$ , but the intercalant stacking sequence is highly faulted, with a correlation length of perhaps only 3 or 4 times  $I_c$ . The correlation length for the graphite sequence is at least  $10I_c$ . Possibly it is much larger, but the widths observed along  $F$  are resolution limited by the rather large mosaic spread ( $6^\circ$  full width at half maximum) of the sample. Scans across lattice rows  $B-E$  in the  $a$  direction give peaks that are instrumentally sharp, indicating a large correlation length for intercalant order within a plane, in agreement with a recent report<sup>4</sup> of high-resolution x-ray diffraction. The stacking sequence implied for the majority phase by the spots in Fig. 1 is  $A\alpha A\beta A\alpha A\beta \dots$ .

The Bragg spots of the minority phase occur at  $(0, l)$  along scan  $A$ ,  $(1/\sqrt{3}, n + \frac{1}{2})$  along  $C$ , and at  $(\sqrt{7}/12, n + \frac{1}{2})$  along  $D$ . There must be another set of spots at  $(1, l)$  along  $F$  due to the minority phase but these are obscured by the intense reflections of the majority phase, because of the large mosaic spread of the sample. The pattern of the minority phase, which has  $I_c = 10.83 \text{ \AA}$ , is, of course, slightly contracted along the  $z$  direction relative to that of the majority phase ( $I_c = 10.24 \text{ \AA}$ ). The assignment of the open diamonds along  $C$  and  $D$  to the minority phase is based on two con-

siderations. First, the intensities are about ten times weaker than the  $B$  and  $E$  reflections, about the same ratio as the intensities of  $(00l)$  reflections for the majority and minority phases (0.93 and 0.07, respectively). Secondly, the peaks along  $C$  and  $D$  show better registry with the lattice parameter  $I_c = 10.83 \text{ \AA}$  than with  $I_c = 10.24 \text{ \AA}$ . Perfect registry is not expected since, as in the case of the majority phase, the stacking sequence is highly faulted, as evidenced by relatively broad peaks in scans  $C$  and  $D$ . These two characteristics can be noted in Fig. 2. Because the neutron beam was masked down to avoid excessive container scattering for scan  $D$ , but not for scan  $E$ , causing a factor of 3 intensity loss, the recorded signal per unit time is about a factor of 30 less for scan  $D$ , rather than a factor of 10 as mentioned above.

The peaks along the  $(1/\sqrt{3}, l)$  lattice row could come from a  $\sqrt{3} \times \sqrt{3}$  triangular superlattice as well as from a  $\sqrt{3} \times 2$  rectangular one, but only the latter can give rise to the  $(\sqrt{7}/12, l)$  reflections, i.e.,  $\frac{7}{12} = (1/\sqrt{3})^2 + (\frac{1}{2})^2$ , involving the lengths of both primitive reciprocal-lattice vectors for the in-plane ordering. It should be noted that a  $\sqrt{3} \times 2$  ordering does not imply a higher intercalant density than a  $2 \times 2$  ordering, since a triangular  $2 \times 2$  layer generates a rectangular  $\sqrt{3} \times 2$  layer by merely shifting a  $(100)$  row of atoms lengthwise by  $a = 2.47 \text{ \AA}$ . Like the majority phase, the minority phase appears to have an  $A\alpha A\beta A\alpha A\beta \dots$  stacking. Our data do not preclude the existence of some small amount of  $\sqrt{3} \times \sqrt{3}$  ordered material in our sample, since all the spots with  $h \leq 1$  generated by such an arrangement would lie on lattice rows  $(1/\sqrt{3}, l)$  and  $(1, l)$ , where they would be obscured by more intense reflections from the other phases.

All the elastic scattering scans  $A-G$  were carried out at 12 K as well as at 297 K. No change was noted in the relative amounts of the two phases, nor was there any indication of phase transitions or improved ordering between 297 and 12 K. The lattice parameters behave qualitatively like graphite or  $\text{KC}_8$  upon cooling,<sup>5</sup> showing a large (2.17%)  $c$ -axis contraction, and a small but significant ( $0.12 \pm 0.03\%$ )  $a$ -axis expansion. Accurate measurements of the C-C bond distance  $d$  for  $\text{KHgC}_4$  were made at 297 K by comparing the position of the  $(100)$  reflection with  $\text{RbC}_8$  and highly oriented pyrolytic graphite (HOPG) samples under the same conditions. For  $\text{RbC}_8$ , we find  $d = 1.4136 \pm 0.0003 \text{ \AA}$ , implying an expansion  $\delta d = 0.0104 \pm 0.0003 \text{ \AA}$  relative to HOPG, in good accord with Nixon and Parry,<sup>6</sup> who reported  $\delta d = 0.01090 \text{ \AA}$  for  $\text{KC}_8$ , and  $\delta d = 0.0103 \text{ \AA}$  for  $\text{CsC}_8$ . For  $\text{KHgC}_4$ , we measure an expansion  $\delta d$  of only  $0.0070 \pm 0.0003 \text{ \AA}$ . According to the interpretation given to  $\delta d$  by Pietronero and Strässler,<sup>7</sup> this implies that the charge transfer from intercalant to graphite in  $\text{KHgC}_4$  is only about 70% of the amount transferred per C atom in  $\text{KC}_8$ ,  $\text{RbC}_8$ , or  $\text{CsC}_8$ . Thus the number of conduction electrons per atom remaining in the intercalant layers is much larger than is typically the case for donor compounds.

Inelastic neutron scattering measurements on  $\text{KHgC}_4$  of phonon dispersion and intercalant modes are summarized in Figs. 3 and 4, respectively. The top two branches in Fig. 3 are due to K vibrations, and lie somewhat lower than K modes in the pure  $\text{KC}_n$  compounds. We assign two branches rather than one at 17 meV because there are two K layers in an intercalate sandwich.<sup>8</sup> The 7-meV mode can be associated primarily with C vibrations, both on the basis

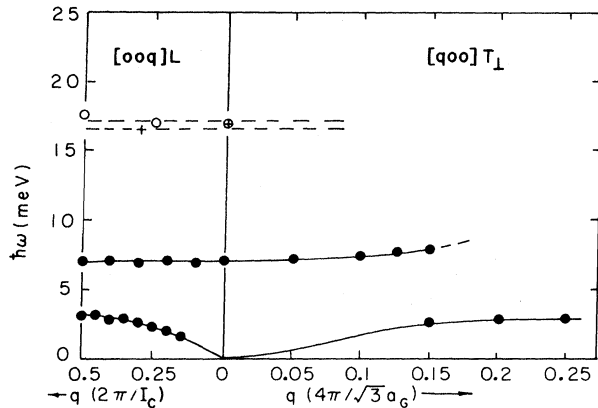


FIG. 3. Phonon dispersion curves for out-of-plane modes.

of the intermediate mass density of the C layers and the high intensities observed for the phonon peaks. The acoustic branch must be collective at small  $q$ , thus involving all atoms, but near the zone boundary, a Hg-like character to the modes is probable, an assignment which is reinforced by the flattening of the  $[100]T_{\perp}$  branch at about the same energy, 3 meV. That is, the massive Hg atoms vibrate essentially as low-frequency decoupled oscillators for out-of-plane motions. The energy for such motions is much less than the 9-meV mean energy of in-plane intercalant modes (Fig. 4). The notation  $[100]T_{\perp}$  is used here to denote basal-plane averaged curves<sup>9</sup> for phonons with  $\bar{q}$  in-plane but displacements out-of-plane. Unlike the case for pure alkali-metal intercalates<sup>10</sup> the in-plane spectrum obtained for  $\text{KHgC}_4$  is not precisely a phonon density of states because the intercalant is not monatomic. Rather, it is dominated by Hg motions because of the larger neutron scattering cross section of Hg (20 vs 1.7 b for K). It would be of interest to perform more phonon measurements on stage-2  $\text{KHgC}_8$ , and on  $\text{KHgC}_4$  samples with predominantly  $\sqrt{3} \times 2$  or  $\sqrt{3} \times \sqrt{3}$  ordering, in order to see if any correlation can be made between the phonon behavior and  $T_c$ .

Our results offer some insight into other factors which influence the peculiar superconducting properties of  $\text{KHgC}_4$ . DeLong *et al.*<sup>1</sup> have previously observed very broad and pressure-sensitive superconducting transitions which extend from onset temperatures  $T_0 \geq 1.4$  K, approximately double the transition temperatures  $T_c = 0.7 - 0.9$  K initially observed by other workers.<sup>2</sup> This unusual behavior has been discussed<sup>1</sup> in terms of possible crystallographic phase mixtures, defects, or potential charge-density-wave instabilities. Subsequent experiments<sup>3</sup> have indeed revealed the presence of multiple phases of  $\text{KHgC}_4$  and sample-dependent  $T_c$  values. Timp, Elman, Dresselhaus, and Tedrow<sup>3</sup> have correlated electron diffraction patterns and  $T_c$  data, concluding that, depending on preparation conditions, four types of

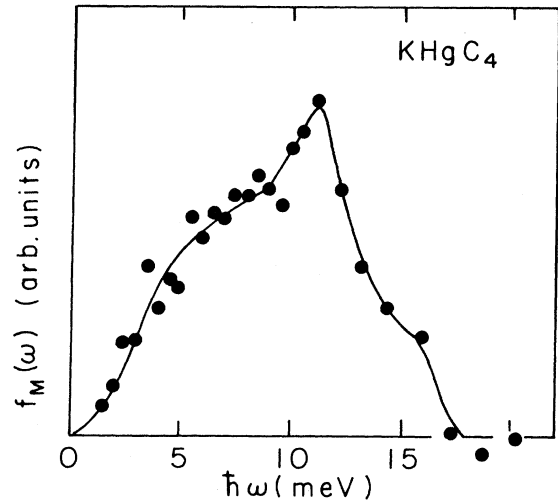


FIG. 4. In-plane intercalant mode spectrum.

intercalant order can be obtained:  $2 \times 2$  triangular ( $T_c = 1.56$  K),  $\sqrt{3} \times 2$  rectangular ( $T_c$  unresolved),  $\sqrt{3} \times \sqrt{3}$  triangular ( $T_c = 1.65$  K), and a disordered structure ( $T_c = 0.75$  K).

Our experiment confirms the existence of the  $2 \times 2$  and  $\sqrt{3} \times 2$  structures, and does not exclude the possible presence of a small amount of  $\sqrt{3} \times \sqrt{3}$  phase. The sharpness of the peaks in  $(00l)$  and  $(hk0)$  scans suggests that the crystallites of both the  $2 \times 2$  and the  $\sqrt{3} \times 2$  phases have dimensions exceeding the reported<sup>2</sup> superconducting coherence lengths ( $\xi \sim 200$  Å in the C direction, and  $\sim 2000$  Å in the a direction), a fact which would not lead one to expect broadening<sup>1</sup> of the superconducting transitions. However, the pressure sensitivity of  $T_c$  and the high density of stacking faults in the intercalant layer registry of  $\text{KHgC}_4$  may provide mechanisms for such broadened transitions. We also note that a very small amount of  $\sqrt{3} \times \sqrt{3}$  phase may have been manifested in the  $T_c$  data of De Long *et al.*, and that this phase may be dominant at high pressures. Experiments to test this possibility, and to characterize the superconducting properties of our neutron diffraction sample, are in progress.

#### ACKNOWLEDGMENTS

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