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Neutron Scattering Studies of Alkali Metal

## Graphite Intercalation Compounds

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Elastic and inelastic neutron scattering are reported for  $C_8Rb$  in the temperature range 4-800 K. Several phase transitions above room temperature are reported for the first time; these consist of changes in metal layer stacking and ultimately at 747 K the onset of 2D liquid behavior. Phonon dispersion of LA and LO modes propagating along  $\bar{c}$  imply a 20% increase in the inter-layer force constant relative to pure graphite. The zone boundary TA mode softens dramatically with increasing temperature, which may be related to the phase transitions.

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Neutron scattering techniques are being applied for the first time to the study of stage 1 alkali metal-graphite intercalation compounds. Elastic neutron scattering is employed to study the structures of these compounds over a wide range of temperatures (4-800 K), thus revealing, for example, the presence of phase transitions between two ordered states. Because of the relative transparency of the compounds to neutrons, neutron diffraction provides a sensitive characterization of the bulk sample as opposed to surface effects. Inelastic scattering can, in principle, be employed to study the dispersion relations for the phonons throughout the entire Brillouin zone. In practice, the only modes that are readily measured are the longitudinal modes propagating along the  $\bar{c}$  direction. However, these modes are quite important as they reflect the interaction between graphite and intercalant layers.

Stage 1 compounds of Cs and Rb were prepared from HOPG<sup>1</sup> (highly-oriented pyrolytic graphite) using the two-temperature method.<sup>2</sup> Samples were typically  $1\text{cm}^2 \times 2-5\text{ mm}$  thick, and were sealed under vacuum in pyrex or quartz ampoules. Measurements were performed at the Brookhaven High Flux Beam Reactor, on either 2- or 3-axis spectrometers. Pyrolytic graphite was used as monochromator, analyzer and filter; the beam collimation was 40 minutes throughout. For all measurements, the  $\bar{c}$  axis was in the scattering plane. The sample holder provided for temperature regulation of  $\pm 3\text{ K}$  in the range 4-800 K.

A schematic reciprocal space diagram for the stage 1 compounds is shown at the top of Fig. 1. The carbon network planes and also planes of metal atoms are all parallel to each other, which leads to well-defined  $(00l)$  reciprocal lattice points along  $\bar{c}^*$ , and intense Bragg reflections represented by the heavy dots. These reflections were used to determine the distance between carbon planes, i.e. 5.64 Å for  $C_8Rb$ , and to confirm that the sample consisted of a uniform stage. For the bulk compounds, HOPG, there is a completely random orientation of the in-plane unit cell vectors about the  $\bar{c}$ -axis.<sup>1</sup> The diffraction intensity is thus spread out into rings about the  $\bar{c}$ -axis, and consequently only a small fraction of this intensity is intercepted by the spectrometer, as in a powder measurement. The smaller dots on the schematic in Fig. 1 represent the series of  $(1,0,l)$  reflections generated by the in-plane carbon atom spacings. The metal atoms form a  $2 \times$  expanded lattice relative to the carbon in-plane network,<sup>3</sup> and give rise to the series of reflections which lie along the line with arrows in the schematic. Reflections observed along this line give information on the  $c$ -axis stacking of the metal layers.

Figure 1 shows the results of diffraction scans on  $C_8Rb$  at several temperatures. For convenience of comparison among graphite and various compounds, in this and succeeding figures  $c^*$  is dimensionless and is given in units of  $2\pi$  divided by the distance along  $\bar{c}$  between successive equivalent carbon planes. The bottom trace at 290 K represents the compound as grown (growth temperature 500 K).

This pattern shows broad maxima which do not peak at simple fractions of  $c^*$ , and, although suggestive of  $\alpha\beta\gamma$  stacking,<sup>4</sup> is more characteristic of a mixture of structures or a disordered state. The middle trace, taken at 721 K, shows that in addition to a sharpening of the Bragg peaks, a phase transition has occurred. The peaks at  $c^* = 0.5$  and  $1.0$  imply an  $\alpha\beta$  stacking of the metal layers. We found no evidence for de-intercalation at 721 K, due presumably to the fact that the compound and its ampoule were at the same temperature. The upper trace was again taken at 290 K, but after several days at 721 K. The pattern is now representative of  $\alpha\beta\gamma\delta$  stacking, with Bragg peaks at  $c^* = 0.25, 0.5$  and  $0.75$  as had been found in early x-ray studies.<sup>3</sup> The structure factor for the  $c^* = 1$  diffraction vanishes.

A more complete set of spectra is shown schematically in Fig. 2. Additional results at 747 K are also shown, in this case indicative of a liquid-like or highly disordered structure for the metal atoms. No transitions were observed below 290 K. In total, then, four different phases were observed for  $C_8Rb$  at and above room temperature. In each case the transitions were not sharp, and the patterns showed a mixture of two phases at some temperatures. Furthermore, the onset temperature for appearance or disappearance of a phase was not reproducible upon cycling the temperature.

These initial results for  $C_8Rb$  can be summarized as follows: a number of different structures exist and it is therefore important to measure the  $(h0l)$  reflections to establish the actual state of the sample. In addition, there are indications that the structure

at a given temperature depends on the thermal history. A totally disordered state for the metal layer is observed for the first time in a stage 1 alkali metal compound.

Similar data for  $C_8Cs$  gave an  $\alpha\beta\gamma$  structure with no phase transition in the range 4-300 K, in agreement with x-ray results.<sup>4</sup> The absence of phase transitions in  $C_8Cs$  and  $C_8Rb$  below room temperature is consistent with transport results.<sup>5</sup> We did not study  $C_8Cs$  above 290 K.

Figure 3 shows for  $C_8Rb$  the phonon dispersion of the LA and LO modes propagating in the c-direction. For comparison, the dashed lines show the corresponding branches in HOPG as measured by Nicklow et. al.<sup>6</sup> In pure graphite the forces between layers are dominated by van der Waals interactions. Electrical<sup>7</sup> and optical<sup>8</sup> data imply an increase in c-axis interaction strength for  $C_8M$  compounds relative to pure graphite. The initial slopes of the LA branches in Fig. 3 can be used to estimate the difference between c-axis force constants of graphite and  $C_8Rb$ . For graphite the actual zone boundary value of  $\bar{c}^*$  is  $2\pi/(2)(3.35) \text{ \AA}^{-1}$  whereas for  $C_8Rb$  the value is  $2\pi/5.64 \text{ \AA}^{-1}$ . Accounting for differences in mass per unit area, we find a stiffening of  $\sim 20\%$  by comparing room temperature data in Fig. 3. This stiffening is also manifested by the increase in frequency of the zone center optic mode. The solid bars at the zone boundary represent rather broad phonon groups that were observed at this wave vector. The mass per unit area of carbon and metal layers are different, which leads to a splitting at the zone boundary as for a one-dimensional

diatomic lattice with unequal masses.

Figure 4 shows the inelastic results for the zone boundary TA mode propagating along  $\bar{c}$ . A dramatic softening of this mode is observed as the temperature is raised, a much larger effect than occurred for the other modes shown in Fig. 3. This softening may be related to the phase transitions observed at high temperature, since the relative shear motion of the TA mode is similar to the atomic displacements which must occur during a change in metal layer stacking.

Although it will be quite difficult to obtain a full set of dispersion relations for these materials because of the complex nature of the reciprocal lattice, these results indicate that useful information on the lattice dynamics of these systems can be obtained and will contribute to improved understanding of their properties.

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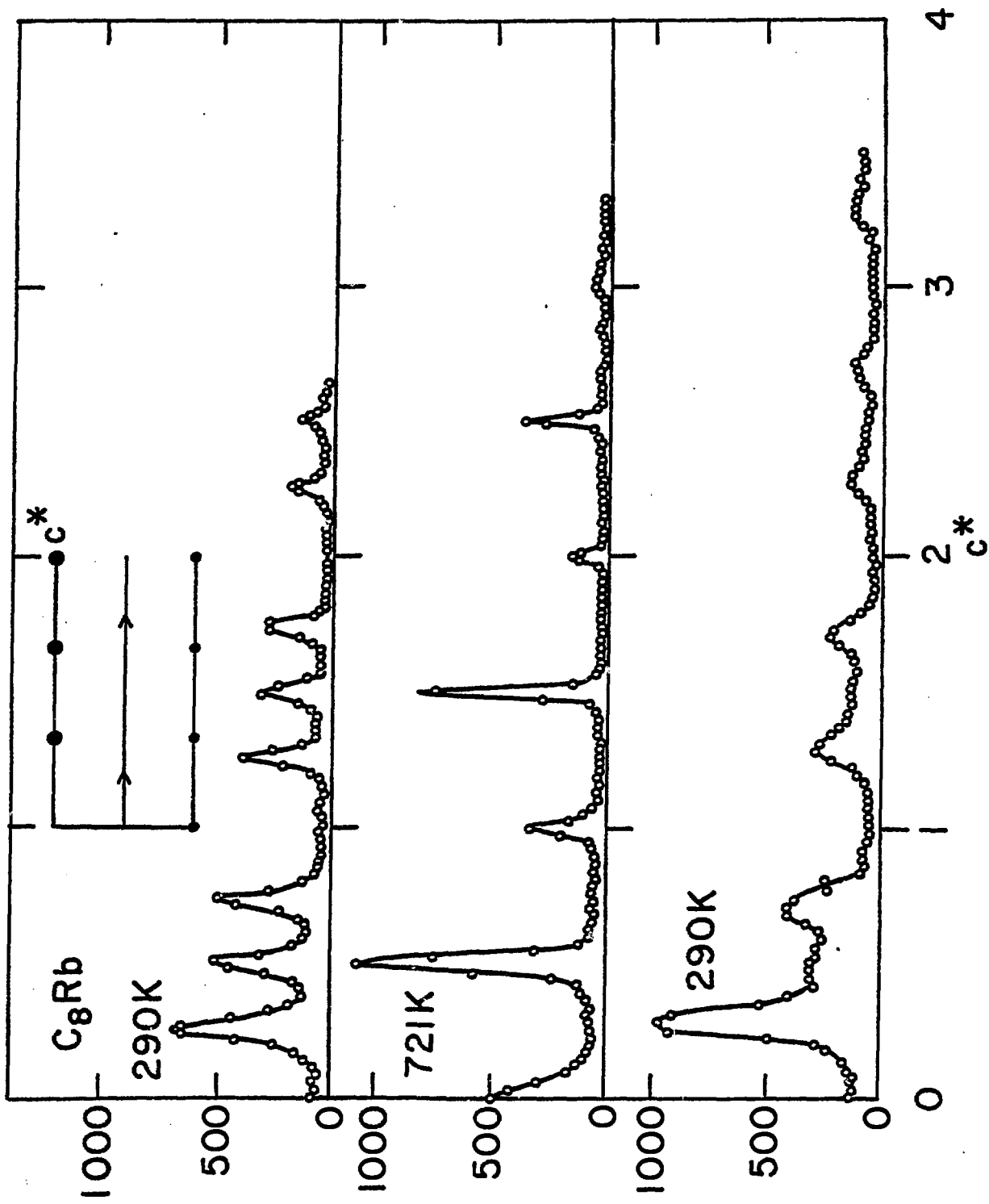
### Figure Captions

Figure 1        Diffraction profiles of  $C_8Rb$  along the reciprocal lattice line indicated in the schematic (see text). The time sequence of the three scans reads from bottom to top.

Figure 2        Reciprocal lattice diagrams of the various structures found in  $C_8Rb$  versus temperature. The time sequence reads from bottom to top.

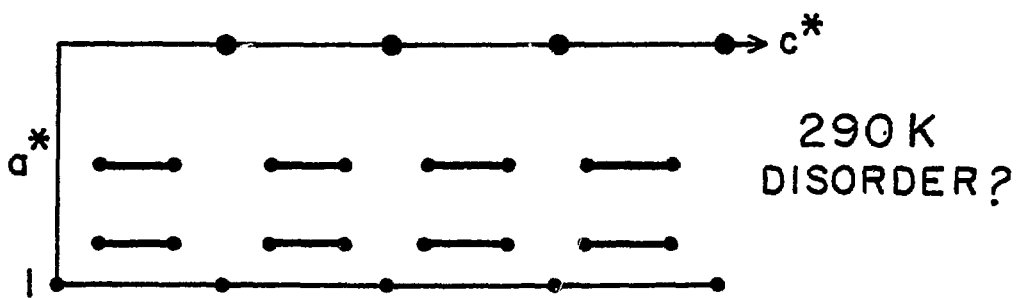
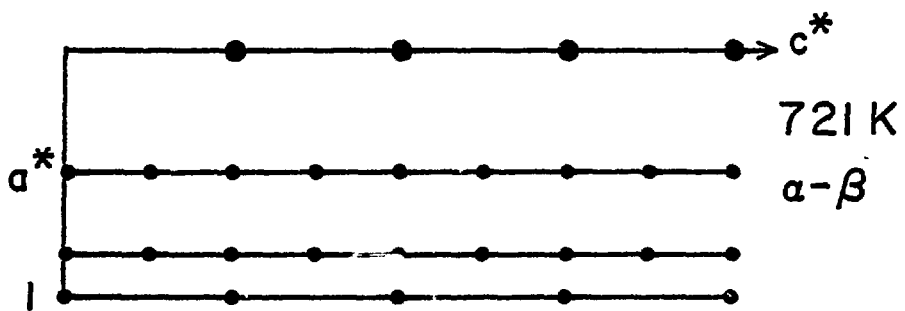
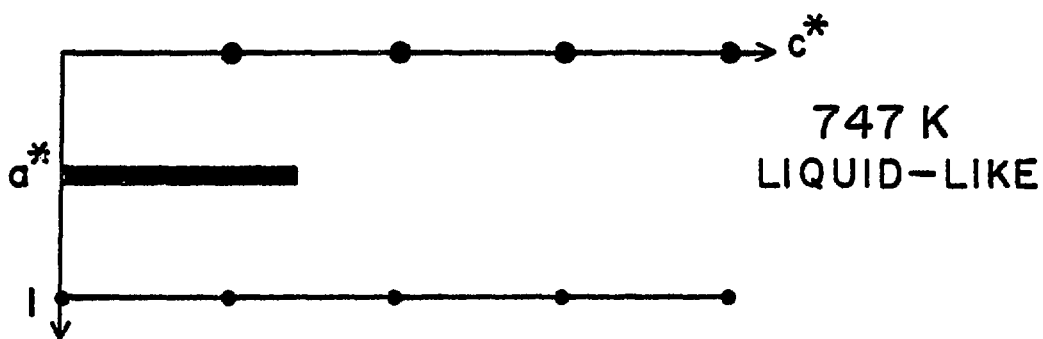
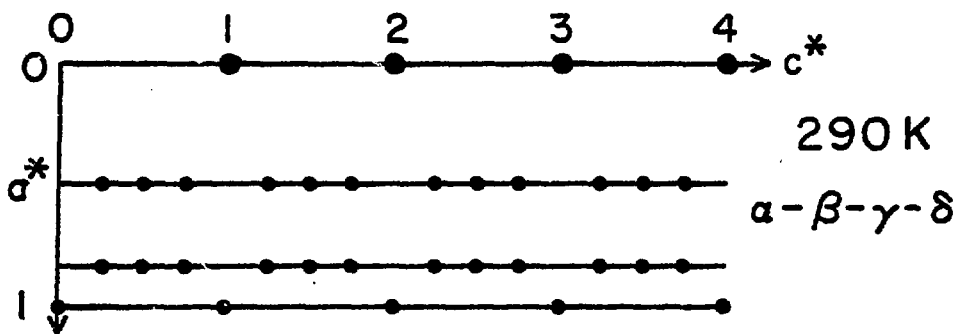
Figure 3        Phonon dispersion of  $RbC_8$  from inelastic scattering, showing the LO and LA modes at 290 K (circles) and 747 K (triangles). Data for pure graphite (dashed lines) is shown for comparison (Ref. 6). The wave vector  $c^*$  is dimensionless, so the curves for graphite and  $C_8Rb$  are not drawn to the same absolute scale (see text).

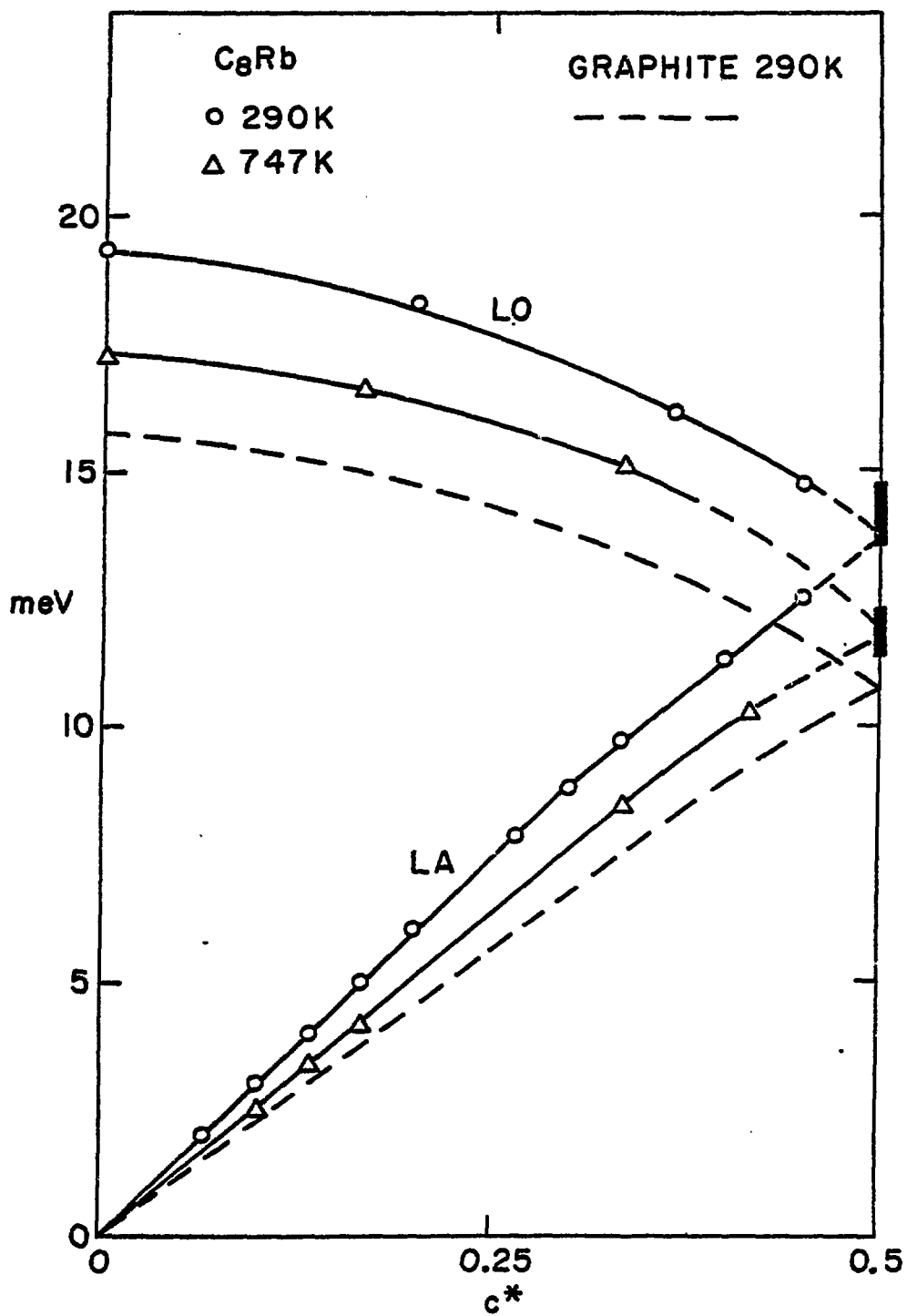
Figure 4        Inelastic spectra for the zone boundary TA mode propagating along  $\bar{c}$ . Note the dramatic softening between 524 K and 747 K (see text). (Points denoted x in bottom trace are simply a repeat scan).





$C_8Rb$





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