

## Phonon Softening in a Mixed Layered System, $K_{1-x}Rb_xC_8$

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By means of inelastic neutron scattering, the dispersion of the longitudinal  $[00q]$  phonon modes has been measured for the first time in the mixed layered compound  $K_{1-x}Rb_xC_8$  over the whole composition range  $0 \leq x \leq 1$ . From the optic and acoustic phonon branches interlayer force constants are derived which are strongly composition dependent. At  $x = 0.65$  the elastic constant  $C_{33}$  shows an anomalous softening of more than 20%, which may be due to a composition-dependent charge transfer between the intercalant and graphite layers.

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There is a substantial and continuing interest in the behavior of phonons in random systems.<sup>1-3</sup> Experimental information of lattice vibrations in these crystals is mainly derived from inelastic-neutron-scattering studies of binary substitutional systems<sup>4-9</sup> and from Raman and infrared spectroscopy of both binary and ternary mixed crystals.<sup>10-13</sup> However, information concerning the phonon dispersion in ternary systems,  $A_{1-x}B_xC$ , over the whole composition region is rather scarce. Here we report the first such study in the mixed graphite intercalation compound  $K_{1-x}Rb_xC_8$ .

Graphite intercalation compounds (GIC's) have proven to be a rich system for the study of phonons in layered compounds, including observations of layer-bending modes<sup>14</sup> and zone-folding effects.<sup>15</sup> GIC's also provide a fertile test ground for the exploration of phonons in layered mixed crystals because the phonon dispersion of the  $c$ -axis longitudinal modes is well known for the pure compounds and can be described by a simple diatomic linear chain model with just two force constants.<sup>16</sup>  $K_{1-x}Rb_xC_8$  is a particularly attractive system since both the in-plane  $2 \times 2$  alkali structure and the  $\alpha\beta\gamma\delta$  stacking sequence are maintained throughout the entire composition region.<sup>17</sup>

Our experiment was performed with use of approximately 12 cm<sup>3</sup> of pyrolytic graphite which was first intercalated to pure  $KC_8$  in a two-bulb glass tube in the usual manner. The sample was then transferred under He atmosphere into a stainless-steel crucible containing Rb metal at the bottom, separated from the sample by a perforated platform. Substitutional intercalation was achieved by heating the sample can to 300°C *in situ* on a neutron dif-

fractometer, and the actual composition was monitored by elastic  $(00l)$  scans. Great care was taken to obtain a homogeneous compound with resolution-limited widths. The  $(00l)$  scans also show an unperturbed long-range periodicity for all compositions of this mixed compound. The substitutional intercalation procedure required about 5-8 h for a 10% change in the binary composition,  $x$ . The composition was determined by use of previous measurements of the interlayer spacing as a function of the binary alkali-metal composition.<sup>17</sup> All of these measurements were performed with a triple-axis spectrometer located at the National Bureau of Standards research reactor. Pyrolytic graphite,  $(002)$  reflection, was used for both the monochromator and analyzer. The inelastic-scattering data were obtained with constant  $\bar{Q}$  scans in both the fixed-initial- and fixed-final-energy configurations, thus assuring peak positions and line shapes. Most inelastic data were recorded at room temperature.

The phonon energies for both the acoustic and optic  $[00q]$   $L$  branches were measured for the compositions  $x = 0, 0.3, 0.45, 0.65,$  and  $0.92$ . A representative example for  $x = 0.45$  is shown in Fig. 1. In each case both branches show appreciable dispersion characteristic of a system in which the vibrational Hamiltonian is replaced by its average. Despite an extensive search for defect modes at several of these concentrations, no evidence for them was observed. For such an average system, the appropriate areal mass density of the alkali layers is given by  $M_A = \frac{1}{8}[(1-x)M_K + xM_{Rb}]$ , where  $M_K$  and  $M_{Rb}$  are the areal mass densities of potassium and rubidium atoms and the factor of  $\frac{1}{8}$  takes into account the overall stoichiometry. Also

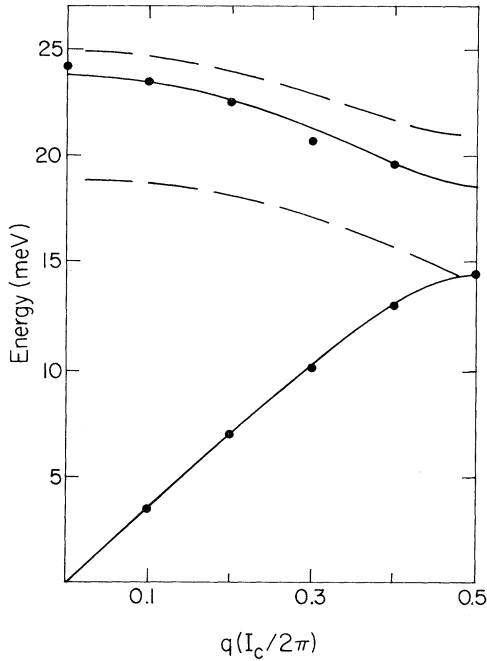


FIG. 1. Measured phonon energies of the longitudinal  $[00q]$  modes in the mixed compound  $K_{0.55}Rb_{0.45}C_8$ . Full lines are best fits with a one-dimensional linear chain model, described in the text. The dashed lines indicate the phonon energies of the optic branches for  $KC_8$  (upper curve) and  $RbC_8$  (lower curve). Similar phonon branches were obtained for the concentrations  $x=0.3, 0.45, 0.65,$  and  $0.95$ . For details see text.

one can expect the vibrational behavior of the averaged system to be similar to that of the nondisordered compounds, which, as mentioned above, have been successfully described by a linear chain model using two force constants.<sup>15</sup> While both force constants,  $\phi_1$  and  $\phi_2$ , have nearly identical values in the pure compounds ( $x=0, 1$ ), a fit of the spectra of the mixed alloys requires the striking compositional dependence shown in Fig. 2. The nearest-neighbor force constant  $\phi_1(x)$  goes through a maximum at  $x=0.5$  while  $\phi_2(x)$ , the second-nearest-neighbor force constant, is negative in the region  $0.3 \leq x \leq 0.85$  with its minimum occurring at  $x=0.65$ . Note that  $\phi_2(x)$  only connects graphite planes across alkali-metal layers (see inset in Fig. 2).

In addition to the evaluation of the force constants, the elastic constant  $C_{33}$  may be deduced from the phonon dispersion via the relation  $C_{33} = v^2 \rho$ , where  $v$  is the initial slope of the acoustic branch and  $\rho$  is the density. Note the dramatic softening at  $x=0.65$  shown in Fig. 3. One can also extract  $C_{33}$  from the best-fit force constants by us-

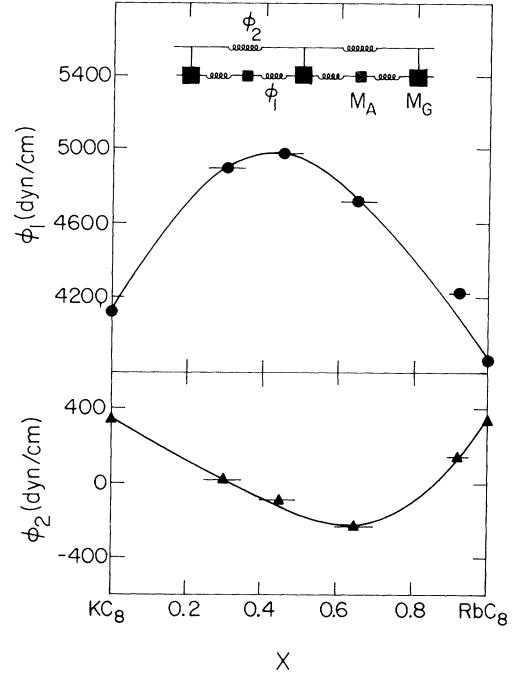


FIG. 2. Composition dependence of the force constants  $\phi_1$  and  $\phi_2$ , describing the phonon dispersion of the longitudinal  $(00q)$  modes in  $K_{1-x}Rb_xC_8$ . The inset schematically sketches the one-dimensional force-constant model used in this study;  $M_A$  and  $M_C$  represent the area-mass densities of the mixed alkali and graphite layers, respectively. The solid line is a guide to the eye.

ing the equation

$$C_{33} = [2I_c(x)/\sqrt{3}a^2][\phi_1(x) + 2\phi_2(x)],$$

where  $I_c(x)$  is the composition-dependent layer separation and  $a = 2.46 \text{ \AA}$  is the graphite basal-plane lattice parameter. This procedure yields the same results as fitting the initial slope directly, indicating that the assumption of composition-dependent force constants is reasonable and that the softening of  $C_{33}$  at  $x=0.65$  is not a singular point but follows naturally from the compositional dependence of  $\phi_1$  and  $\phi_2$ .

We have also noticed that the intensity of the phonon group at  $Q = 2.6[I_c(x)/2\pi]$  vanishes for the composition  $x=0.65$ . This finding, which is not predicted by a harmonic structure-factor calculation, parallels independent observations of anomalies in the magnetic susceptibility<sup>18</sup> and in the width of the  $(002)$  Bragg reflection<sup>17</sup> for the same composition. An extensive search for alkali-layer superordering and stacking rearrangement at the composition in question did not reveal any structural effects which could explain the observed elastic

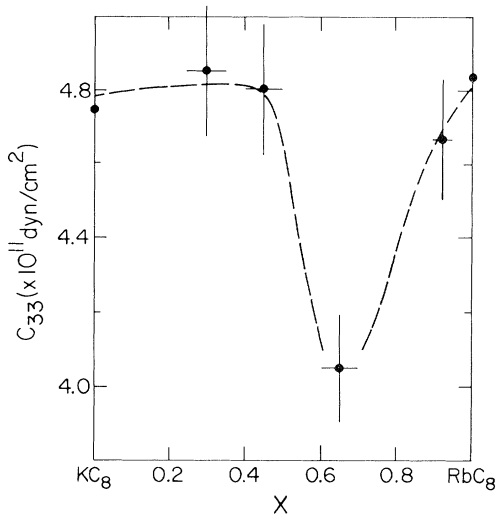


FIG. 3. Composition dependence of the elastic constant  $C_{33}$ , derived from the initial slope of the acoustic-phonon branch. Dashed line is a guide to the eye.

softening. We have also studied the temperature dependence of the phonon energies for the  $x = 0.65$  sample up to 600 K without finding any anomalous temperature effect. We are therefore led to suggest that the composition dependence of the force constants,  $\phi_1$  and  $\phi_2$ , is caused by a composition-dependent charge transfer between the mixed alkali layers and the graphite layers. In the pure compounds  $\text{KC}_8$  and  $\text{RbC}_8$  the fractional charge transfer between alkali-intercalant and graphite layers is believed to be identical and about 0.8 to 1.0 electrons per alkali atom.<sup>19-21</sup> However, the effective charge transfer per individual alkali atom in the mixed compound may show large fluctuations, depending on the average layer separation and the short-range elastic distortion field present around each atom. For instance, a defect Rb atom compressed in a nominal K layer exhibits a different (presumably larger) charge transfer than in a pure  $\text{RbC}_8$  compound. In addition, the rate at which the charge transfer changes with  $x$  must be different for K and Rb in order to produce the slight deviation from a symmetric functional behavior in the force constants. The same charge-transfer asymmetry also may be responsible for the off-center cusp in the magnetic susceptibility,<sup>18</sup> the asymmetric change of the layer spacing with composition,<sup>17</sup> and recently observed Raman-scattering anomalies<sup>22</sup> in this system.

As mentioned above, we have not observed inelastic neutron scattering attributable to local or gap modes associated with the substantial defects. However, while we cannot completely rule out their

existence, we again remark that the optic band exhibits appreciable dispersion for all compositions studied in contrast to what could be expected from a composition-dependent crossover between local or gap-mode and band-mode behavior. We also note that the Chang-Mitra condition for two-optic-branch behavior,<sup>23,24</sup>  $M_K < \mu_{\text{Rb,C}}$  ( $\mu$  is reduced mass), is only marginally satisfied in  $\text{K}_{1-x}\text{Rb}_x\text{C}_8$  with  $M_K = 4.87$  and  $\mu_{\text{Rb,C}} = 5.62$ .

In conclusion, we have measured for the first time the phonon dispersion of the mixed graphite intercalation compound  $\text{K}_{1-x}\text{Rb}_x\text{C}_8$  over the whole composition region. We have observed a striking softening of the elastic constant  $C_{33}$  for the composition  $x = 0.65$  and propose that this softening is electronically driven by a composition-dependent charge transfer between the mixed alkali layers and graphite layers. Force constants which are strongly dependent on the composition have also been extracted from the measured  $[00q]$  longitudinal optic and acoustic phonon branches.

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simpler visualization.

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