Phonon-Raman Anomaly in the Ternary Graphite Intercalation Compound $K_{1-x}Rb_xC_8$

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We report the first measurements of the Raman spectra of an alkali ternary-solid-solution graphite-intercalation compound $K_{1-x}Rb_xC_8$, $0 \leq x \leq 1$. A broad asymmetric softening of the graphite *M*-point phonon modes is observed at $x \approx 0.67$. This anomaly is attributed to electronic band-structure modifications which alter the electron-phonon contribution to the phonon self-energies and which result from the formation of KRb_2-like clusters.

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The alkali ternary-solid-solution graphite intercalation compounds (GIC's) $M_{1-x}M'_xC_8$, $0 \leq x \leq 1$, M,M' = K, Rb, or Cs, were first synthesized about a decade ago by Furdin, Carton, Herold, and Zeller.[1] They characterized the stage-1 structure and found, but did not explain, an anomalous peak in the *x* dependence of the magnetic susceptibility of $K_{1-x}Rb_xC_8$ at $x \approx 0.67$. More recently, Neumann *et al.*[2] showed from neutron scattering studies of the *interlayer* phonons that $K_{1-x}Rb_xC_8$ also exhibits anomalous softening of the C_{33} force constant at $x \approx 0.67$. They attributed the *interlayer* phonon anomaly and the peak in the magnetic susceptibility to the composition dependence of the charge transfer from the mixed alkali layers to the graphite layers. However, more recent x-ray studies of the *x* dependence of the *intraplanar* C-C bond distance[3] reveal a constant bond length. This indicates that charge transfer may be an ingredient of but not the central feature in the complex mechanism which is responsible for the $x \approx 0.67$ anomaly.

In this Letter we report the first Raman studies of an alkali ternary-solid-solution GIC. We will show that the *M*-point *intraplanar* optic phonons[4] of $K_{1-x}Rb_xC_8$ also show a dramatic asymmetric softening and linewidth enhancement at $x \approx 0.67$. More importantly we suggest that the $x \approx 0.67$ anomalies result from electronic band-structure alterations that are associated with the formation of KRb_2-like clusters.

Samples of $K_{1-x}Rb_xC_8$, $0 \leq x \leq 1$, of typical dimension $3 \times 4 \times 0.5$ mm^3, were prepared from highly oriented pyrolytic graphite by sequential intercalation of rubidium and potassium (in that order) by use of the standard two-bulb method.[5] Details are given elswhere.[6] The composition, *x*, was determined from x-ray measurements of the relative intensities of the (001) and (002) reflections.[6] All specimens studied here were homogeneous pure stage-1 compounds as determined from (00*l*) x-ray diffraction studies. The polarized Raman spectra reported here were acquired at room temperature with 5145-Å argon-laser excitation, backscattering geometry, and a cylindrically focused line image (< 30 mW) to eliminate radiation-induced desorption. In order to accurately measure the *M*-point phonon frequencies, all spectra were directly referenced to the 5286.08-Å Ar fluorescence line which was allowed to "leak through" as an internal calibration standard.

The polarized Raman spectra of $K_{1-x}Rb_xC_8$ are shown for the region of the *M*-point phonons (400 − 600 cm^{-1}) for several values of *x* in Fig. 1. Full scans over the range 0 − 2000 cm^{-1} have been acquired for each specimen. These scans, which will be discussed in detail elsewhere,[7] have the qualitatively unique characteristics of the spectra of stage-1 alkali binary GIC's.[8] In particular, there is no evidence in any of the acquired spectra for a stage-2 or higher-state phase in the surface region ($\approx$ 1000 Å deep) probed in the Raman process. Also, surface scans revealed a lateral spatial homogeneity on a scale of $\lesssim 50$ μm.

We focus here on the *M*-point phonons because they constitute the sharpest Raman feature, the composition dependence of which can be readily monitored. For the polarization configuration of Fig. 1, the peak at ≈ 570 cm^{-1} is associated with the $A_g + B_{1g}$ modes of the D_{2h}^{24} space group of the ordered binary GIC's KC_8 or RbC_8.[4,9] This peak is Fano broadened[10] as a result of the interaction between the discrete phonon state and a one-

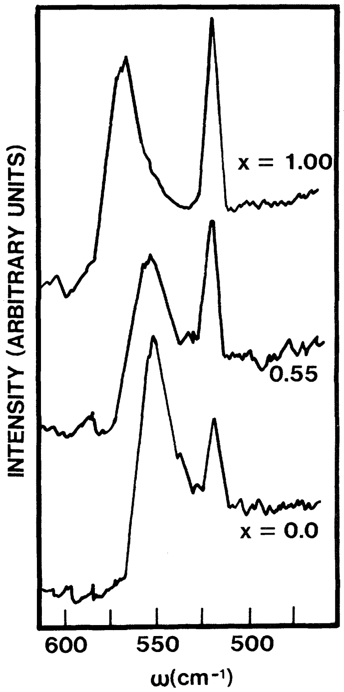

FIG. 1. Raman spectra of $K_{1-x}Rb_xC_8$ recorded with both incident and scattered photons polarized parallel to the scattering plane. The sharp feature at 517.37 cm^{-1} corresponds to the 5286.08-Å Ar^+ emission line (see text).

phonon continuum background.[11]

In Fig. 2 we show the x dependence of the renormalized phonon frequencies which are obtained directly from the peak positions in Fig. 1 while in Fig. 3 we show the corresponding x dependence of the linewidth (full width at half maximum) determined empirically from Fig. 1 by a standarized procedure that takes consistent account of the background. The most noticeable feature of Fig. 2 is the striking asymmetric phonon softening at $x \approx 0.67$. This behavior is mimicked by the phonon linewidth (see Fig. 3) which exhibits an asymmetric maximum at $x \approx 0.67$. It is clear from Figs. 2 and 3 that the M-point phonons of $K_{1-x}Rb_xC_8$ exhibit a one-mode behavior[12] with the variation of x. To our knowledge, the bizarre composition dependence of Figs. 2 and 3 may be unique to the alkali ternary GIC's.

To understand the Raman data presented here we must consider first the species dependence of the M-point phonon modes in the alkali binary GIC's. Note that although the masses of K, Rb, and Cs obey the relation $M_{Cs} > M_{Rb} > M_K$, the observed M-point modes of KC_8, RbC_8, and CsC_8 have frequencies which obey the relation $\omega_{Cs} > \omega_{Rb} > \omega_K$.[9]

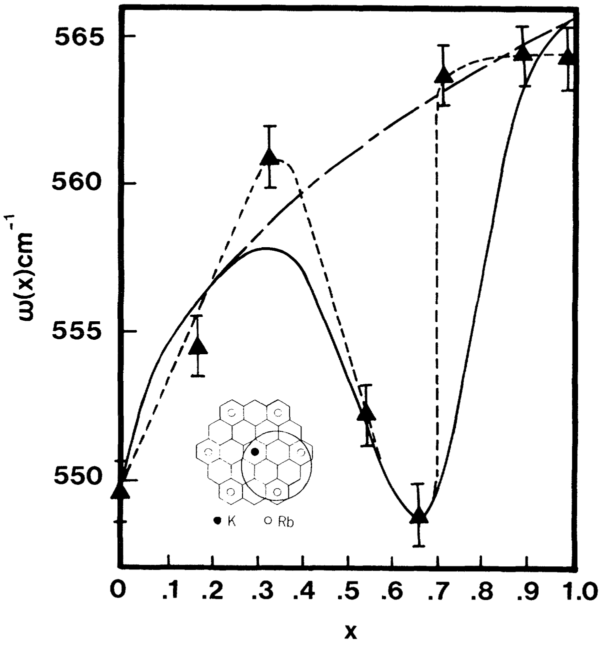

FIG. 2. The x dependence of the $A_g + B_{1g}$ phonon energy (triangles) for $K_{1-x}Rb_xC_8$ obtained from the data of Fig. 1. The dashed line is a guide to the eye through the data. The broken line is a plot of the first two terms in Eq. (1) of the text while the solid line is a plot of Eq. (1). The inset at the lower left shows the $(2\sqrt{3}\times 2\sqrt{3})R30°$ KRb_2 superlattice structure (see text) with a three-atom KRb_2 cluster encircled.

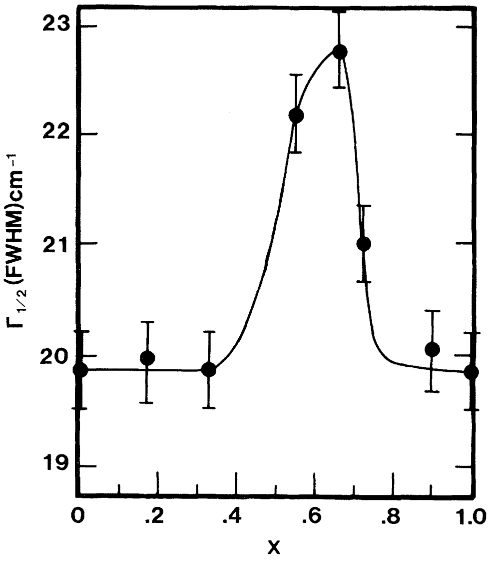

FIG. 3. The x dependence of the $A_g + B_{1g}$ phonon linewidth (circles) obtained from the data of Fig. 1. The solid line is a guide to the eye.

Thus, the species-dependent frequency shift must be associated with changes in the force constants which determine the mode frequency, and not with changes in the intercalant mass. In further support of this concept we note that the eigenvectors for the $A_g + B_{1g}$ mode involve out-of-plane displacements of the carbon atoms only while the intercalant atoms remain undisplaced.[4]

The phonon energy of any solid is primarily a manifestation of two terms in the potential-energy function. One, $V(\vec{R})$, results from interatomic interactions and one, $V_{\text{e-ph}}(\vec{r})$, is due to electron-phonon interactions which renormalize the phonon energies and depend on the electronic states of the system, i.e., on the electronic band structure. Here, $\vec{R}$ and $\vec{r}$ are relative nuclear and electron coordinates, respectively. The species-dependent increase in the effective force constant of the M-point modes of binary alkali GIC's has been attributed to changes in $V(\vec{R})$ that result from an increase in the guest-host interaction as the size of the guest ion is increased and the equilibrium distance between it and its nearest neighbors decreases.[13] Such an explanation is quite plausible if applied to the pure binary MC_8 compounds. However, its application to the ternary $M_{1-x}M'_xC_8$ GIC's would result in M-point modes which vary *continuously* and smoothly from ω_M and $\omega_{M'}$ as x varied from 0 to 1 unless $V(\vec{R})$ is discontinuously perturbed by, for example, a disorder-order transition in the structure of the intercalant layer.

The most probable ordered structure which one might associate with the $x \approx 0.67$ anomalies is a $(2\sqrt{3} \times 2\sqrt{3})R30°$ KRb_2 superlattice, the local configuration of which is shown in the inset of Fig. 2. A careful x-ray diffraction study[3] of a sample with composition $x = 0.65$ failed to reveal any evidence of KRb_2-like long-range ordering or of any other in-plane ordering.[14] Furthermore, a disorder-order–induced perturbation to $V(\vec{R})$ would be expected to yield a sharp anomaly at $x = 0.67$ in contrast to the broad extended feature seen in Fig. 1. Therefore, we do not associate the $x \approx 0.67$ anomalies with the composition dependence of $V(\vec{R})$.

We attribute all of the $x = 0.67$ anomalies (Raman, neutron,[2] and magnetic susceptibility[1]) to changes in electronic structure that are caused by the formation of small (≈ 3–7 atoms) KRb_2-like clusters which will be statistically most numerous for $x = 0.67$. It is well known[15] that small clusters of as few as 3–8 correlated atoms in a solid whose x-ray diffraction pattern shows no evidence of long-range order can nevertheless give rise to features in the density of electronic states that characterize the cluster correlations. Accordingly, small KRb_2-like clusters could alter the electronic band structure of $K_{1-x}Rb_xC_8$ in such a way that the electron-phonon coupling term leads to a lowering of the $A_g + B_{1g}$ phonon self-energy. Since the band structure will depend on the presence of such clusters, i.e., on x, so too will the phonon self-energies. Note also that the pronounced phonon softening of ≈ 10 cm^{-1} (see Fig. 2) is nevertheless small, as expected, compared to the ≈ 80-cm^{-1} contribution of the electron-phonon interaction to the 1580-cm^{-1} graphite mode of alkali binary GIC's.[16]

The smallest cluster possessing the necessary stoichiometry is an equilateral triangle the sides of which have a length equal to the distance between nearest occupied carbon hexagon centers and the corners of which contain one K ion and two Rb ions (see inset in Fig. 2). If we assume that K-K, K-Rb, and Rb-Rb bonds are equally likely, then the number of three-ion KRb_2 clusters present in our specimens will be proportional to $(1-x)x^2$. The rhombohedral primitive cell of a KRb_2 $(2\sqrt{3} \times 2\sqrt{3})R30°$ superlattice contains only one KRb_2 unit, but incorporates four K atoms and thus requires at least four clusters to be defined. The number of such cells is approximately proportional to $[(1-x)x^2]^4$. This function, like the data of Fig. 2, is asymmetric about the $x = 0.67$ inflection point. We model the change in the $A_g + B_{1g}$ frequency as a result of the $V(\vec{R})$ term as a harmonic interaction,

$$\omega(x) = \omega_0 + [k_0 + k_{\text{Rb}} + k_{\text{K}}(1-x)],^{1/2}$$

where k_0, k_{Rb}, and k_{K} are effective carbon, rubidium, and potassium force constants, and ω_0 is an arbitrary reference frequency. Then $\omega(x) = 549.5 + 16|x^{1/2}|$ cm^{-1} yields a reasonable fit to the data of Fig. 2 provided we exclude the range of the dip $0.3 \leqslant x \leqslant 0.67$. To zeroth order, the softening associated with $V_{\text{e-ph}}$ will be proportional to $-[(1-x)x^2]^4$; thus we estimate $\omega(x)$ as

$$\omega(x) = 16|x^{1/2}| + 549.5 - 2.87 \times 10^4[(1-x)x^2]^4. \tag{1}$$

This function is shown as the solid line of Fig. 2 and is in qualitative agreement with the data which, however, show a somewhat sharper feature at $x \approx 0.67$. [While other pairs of nonlinear functions may produce an equally good fit to the data of Fig. 2, Eq. (1) is justifiable on physical grounds.] The softening of the *interlayer* phonons previously reported[2] can of course also result from cluster-induced changes in the appropriate electron-phonon coupling term while the anomaly in the magnetic susceptibility[1] is naturally accounted for by changes in the density of states at the Fermi level caused by cluster-induced band-structure alterations.

The associate of the $x = 0.67$ anomalies with KRb_2-like clusters, though plausible and intriguing, is admittedly somewhat speculative. It could be definitively tested with a phonon self-energy calculation that employs, for example, coherent-potential-approximation (CPA)-derived x-dependent band structures including cluster effects. Hopefully, the data presented here will stimulate such calculations.

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[1] G. Furdin, B. Carton, A. Herold, and C. Zeller, C. R. Acad. Sci. Ser. B **280**, 653 (1975).

[2] D. A. Neumann, H. Zabel, J. J. Rush, and N. Berk, Phys. Rev. Lett. **53**, 56 (1984).

[3] P. Chow and H. Zabel, to be published.

[4] P. C. Eklund, G. Dresselhaus, M. S. Dresselhaus, and J. Fisher, Phys. Rev. B **16**, 3330 (1977); C. Horie, M. Maeda, and Y. Kuramoto, Physica (Utrecht) **99B**, 430 (1980).

[5] A. Herold, Bull. Soc. Chim. Fr. **1955**, 999.

[6] P. Chow and H. Zabel, Synth. Met. **7**, 243 (1983).

[7] S. A. Solin, P. Chow, and H. Zabel, to be published.

[8] S. A. Solin, Physica (Utrecht) **99B**, 443 (1980).

[9] S. A. Solin, and N. Caswell, J. Raman Spectrosc. **10**, 129 (1981).

[10] U. Fano, Phys. Rev. **124**, 1866 (1961).

[11] N. Caswell and S. A. Solin, Phys. Rev. B **20**, 2551 (1979).

[12] I. F. Chang and S. S. Mitra, Phys. Rev. **172**, 924 (1968).

[13] M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).

[14] There is also no evidence to data for a KRb_2-ordered phase of the bulk binary metallic alloy.

[15] D. Weaire, M. F. Thorpe, and V. Heine, J. Non-Cryst. Solids **8–10**, 128 (1972).

[16] H. Miyazaki, T. Hatano, G. Kusunoki, T. Watanabe, and C. Horie, Physica (Utrecht) **105B**, 381 (1981).