

Comment on Anomalies in $K_{1-x}Rb_xC_8$

H. Zabel

Ruhr-University Bochum, Bochum, FRG

The mixed stage 1 graphite intercalation compound $K_{1-x}Rb_xC_8$ has recently been the subject of much interest because of the anomalies which have been reported to occur as a function of the composition x . Chow and Zabel [1] have shown that for the entire composition range the alkali-metal atoms are located in registry over carbon hexagons, forming a $(2 \times 2) RO^\circ$ in-plane structure with complete site disorder of the K and Rb atoms. In addition, the $\alpha\beta\gamma\delta$ stacking sequence of the alkali-metal intercalate layers is maintained for all compositions x .

The anomalies concern the interlayer spacing, the paramagnetic susceptibility, and some phonon modes. Those will be discussed separately further below.

Billaud and Hérold [2] showed for the first time a striking anomaly of the c -axis repeat distance I_c normal to the layers as a function of the composition x , characterized by small slopes at small and large x , and a steep slope at about $x \approx 2/3$. Strong deviations from Vegard's law were also observed in the compounds $Rb_{1-x}Cs_xC_8$ and $K_{1-x}Cs_xC_8$, but with the strongest deviations at different compositions x . Chow and Zabel [1,3] repeated these experiments and obtained results in qualitative agreement with the earlier measurements by Billaud and Hérold, although the samples, the intercalation procedure, and the analysis of the composition were quite different. Billaud and Hérold [2] used powder graphite as host material, they intercalated their samples by the vapor phase from a premixed alkali-metal alloy, and determined the final composition of the intercalated compound by spectroscopic means. In contrast, Chow and Zabel [1,3] used HOPG material, which was first intercalated to pure RbC_8 , followed by a substitutional reaction via exposing the RbC_8 sample to K vapor. The substitution was monitored in-situ by x -ray $(00l)$ scans and the c -axis repeat distance I_c , as well as the composition were obtained from the position and the intensity of the $(00l)$ Bragg-reflections, respectively. This method guarantees that the alkali-metal composition is determined only from the structurally coherent parts of the host lattice.

Another, similar experiment was recently reported by Medjahed et al. [4] on samples derived from single crystals. In contrast to the earlier work, Medjahed et al. [4] found a linear dependence of the interlayer spacing I_c on x (Vegard's law). These authors propose that the different results are due to the different host materials used, and that single crystals with a smaller amount of structural defects, such as voids, result in a linear c -axis variation. In other words, the anomalies observed on HOPG based material were claimed to be due to lattice inhomogeneities of the host material.

In a subsequent single crystal study, Chow and Zabel [1] showed that the interlayer spacing can be determined precisely by the x -ray $(00l)$ reflections, however, that the determination of the composition from the x -ray structure factor is hampered by unknown Debye-Waller factors and elastic distortion fields which have a drastic effect on the x -ray intensities. Keeping these difficulties in mind, the error bar for the composition is at best $\Delta x = \pm 0.1$, which is on the same order of magnitude as the reported deviation from the linear slope. In conclusion, at the present state it remains undecided whether there exists

a deviation from Vegard's law in $K_{1-x}Rb_xC_8$ or not. The HOPG and single crystal results of Chow and Zabel are shown in Fig. 1.

Along with the anomaly in the interlayer spacing, Furdin et al. [5] reported a striking dependence of the paramagnetic susceptibility on the composition, peaking also at $x = 2/3$. However, later experiments by Chow et al. [6] have not been able to confirm these results.

Neutron scattering studies of the [00q] longitudinal phonon dispersion (layer breathing modes) by Neumann et al. [7] revealed an anomalous softening of the layer compressional elastic constant C_{33} at the composition of $x = 2/3$. The elastic constant was derived from a fit of the phonon dispersion to a simple force constant model, as well as from the initial slope of the acoustic branch. Both methods yielded consistently the same results. Solin et al. [8] reported Raman data on the M-point intralayer $A_g + B_{1g}$ mode, which also indicates anomalies of the Raman shift as well as the linewidth, both centered at $x = 2/3$. Mejahed et al. [4] have re-examined the composition dependence of the Raman spectra on single crystals of $K_{1-x}Rb_xC_8$ and conclude that the Raman phonon anomaly is an artefact, possibly due to structural defects in synthetic graphite materials. However, the M point phonon frequency exhibits a highly non-linear composition dependence with the maximum deviation from linearity occurring in the range $0.6 < x < 0.7$ even in the single crystal based sample. This renormalization of the phonon frequency in the range $0 < x < 0.6$ may still qualify as an anomalous behavior, although the 'dip' in the Raman frequency may not be as deep as suggested in the original data reported by Solin et al. [8].

Akera and Kamimura [9] pointed out that the elastic anomalies may be understood by a band structure effect. In KC_8 the three-dimensional alkali-metal band at the Γ point is placed above the Fermi level, whereas in RbC_8 the equivalent band is placed below the Fermi level, all other band structure features being topologically very similar in both compounds. Therefore, by changing the composition x , the interlayer spacing increases, moving the Fermi level from below to above the upper alkali metal s-band. At the composition $x = x_c$ the Fermi level touches the 3D alkali-metal band causing a cusp-shaped Van Hove singularity to occur in the electron density of states for this composition. This singularity, in turn, is responsible for the elastic anomaly in the ternary $K_{1-x}Rb_xC_8$ compound. The occurrence of an anomaly in the elastic properties of the ternary compound therefore sheds light on the band structure of KC_8 and RbC_8 , and provides proof that in KC_8 the Fermi level is situated below the upper alkali-metal derived band. The position of the Fermi level has given rise to much controversy in recent years (see Holzwarth [10]).

Recently, Chow and Zabel [1] have reported high resolution x-ray measurements of the carbon-carbon bond length. It is well known that the bond length is a sensitive measure of the charge transfer between intercalate bands and bounding graphite Π bands, which, in turn, is sensitive to the position of the Fermi level. In their measurement, Chow and Zabel have not been able to observe any significant change in the carbon-carbon bond length as a function of the composition x (Fig. 2). This negative result could be interpreted as an indication for a lack of variation of the Fermi level as a function of x . Another plausible reason for the composition independence of the bond length may be seen in a cancellation effect: buckling of the graphite planes due to the different K and Rb ion sizes on one hand, and composition dependent charge transfer on the other hand, may lead to an unchanged projection of the bond length into the direction of the layers. However, recent EXAFS

measurements of the local bond length in the ternary compound by Krone et al. [11] has not revealed any changes of the $K - C$ or $Rb - C$ distances in the ternary compound, leaving some doubt towards the buckling idea of the graphite planes.

In conclusion, the ternary compound $K_{1-x}Rb_xC_8$ exhibits some anomalies as a function of x , most notably in the layer compressional elastic constant C_{33} , which shows a softening of about 20 % at $x = 2/3$. This anomaly may be attributed to a band structure effect as pointed out by Akerá and Kamimura. All other anomalies reported earlier and concerning the interlayer spacing variation, the softening of the Raman M point frequency, and the paramagnetic susceptibility are either less pronounced or even doubtful. However, even in the case that the interlayer spacing varies linearly, an anomaly in C_{33} would still be expected, but the softening would be somewhat less deep (see contribution by H. Kamimura in this volume). On the other hand, the missing change of the carbon-carbon bond length from KC_8 to RbC_8 causes a bit uneasy feelings.

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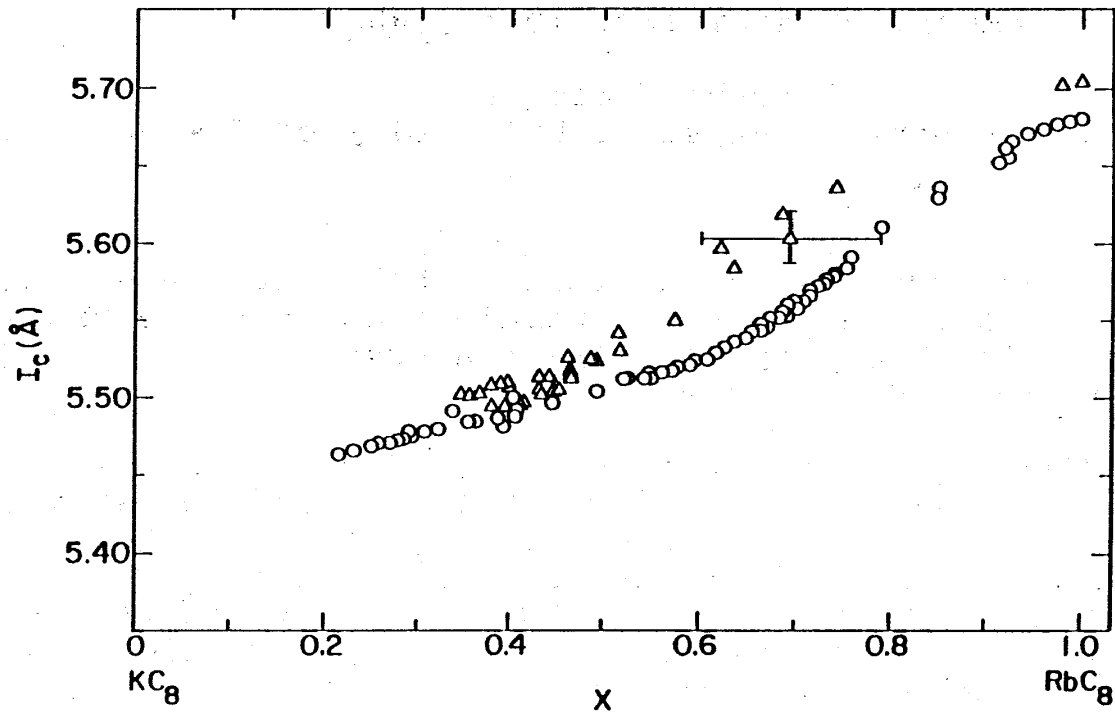


Fig. 1 The layer separation I_c versus composition x in $K_{1-x}Rb_xC_8$ measured in situ on samples at 250 C. Open circles are for measurements based on HOPG, and triangles are for single crystal measurements. (From Ref. 1)

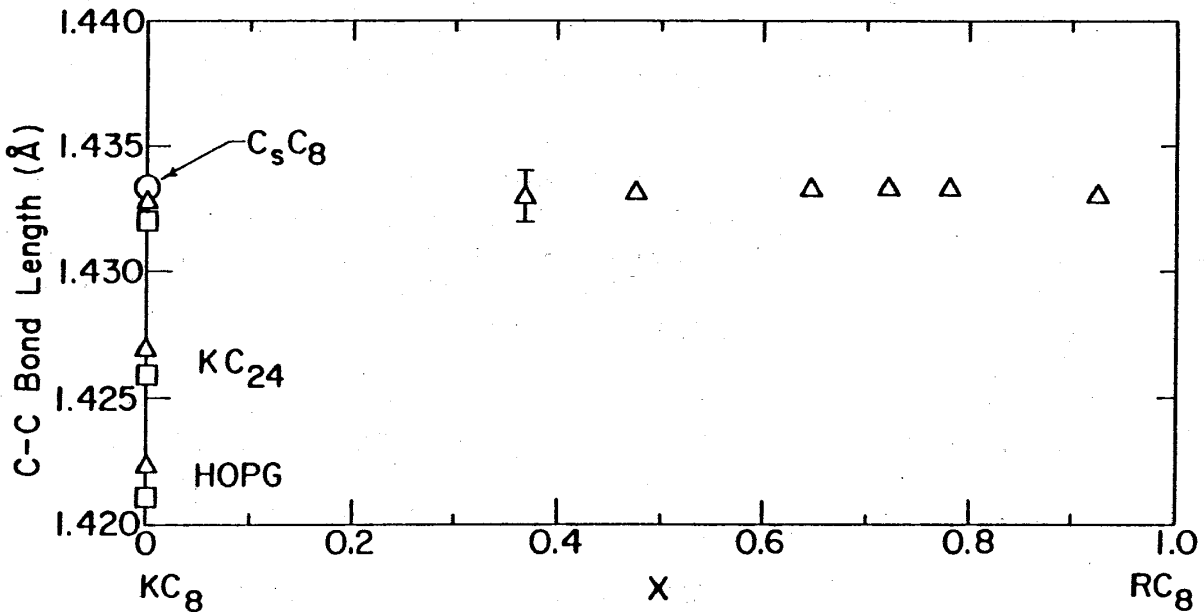


Fig. 2 The carbon-carbon bond length in pristine graphite, and in stage 1 and 2 alkali intercalation compounds. Triangles show the bond length as a function of the ternary composition x in $K_{1-x}Rb_xC_8$. (From Ref. 1)