Thermal expansion and lattice anharmonicity of alkali-graphite intercalation compounds

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We have measured the c-axis and a-axis thermal expansion of several alkali-metal—graphite intercalation compounds by means of x-ray scattering between 10 and 300 K. The c-axis thermal expansion depends strongly on the in-plane mass density of the alkali-metal atoms and the stage of the compound, and is largest for KC_8. The a-axis thermal expansion of KC_8 and KC_{24} is negative in the considered temperature region and the room-temperature coefficient is twice as large as for pristine graphite. We have analyzed the c-axis data in terms of a one-dimensional quasiharmonic approximation, which yields Grüneisen parameters 2 or 3 times as large as those for graphite.

I. INTRODUCTION

The highly anisotropic properties, unusually large anharmonicity and very high melting temperature of graphite has caused a continuing interest in the study and comparison of the thermal expansion of the many forms of graphite materials.[1,2] The anisotropy is manifested in the layered-type structure of graphite having a strong covalent SP^2 bonding between carbon atoms in the layers and a considerably weaker van der Waals coupling between the layers. Accordingly, the thermal expansion of graphite is highly anisotropic, being large $(2.4 \times 10^{-5}/\text{K})$ and positive normal to the layers, but very small and slightly negative parallel to the layers.

The harmonic and anharmonic properties of graphite can artificially be changed by inserting monatomic layers of alkali atoms between graphite basal planes. In these alkali-metal—graphite intercalation compounds (AGIC's), the graphite and alkali planes form a well-ordered periodic sequence along the axis, and the compounds are labeled by the stage n, where n designates the number of graphite planes between any two consecutive alkali-metal planes. The influence of changed masses, symmetries, and interaction potentials has been demonstrated in a number of experiments studying the conductivity, optical, vibrational, and elastic properties of graphite intercalation compounds.[3] Here, we focus on the effect intercalation has on the anharmonic properties of graphite, by measuring the a- and c-axis thermal expansion of AGIC's.

Our interest in this study was stimulated by the fact that the longitudinal phonon modes propagating along the c-axis direction can be successfully described by a one-dimensional lattice-dynamical model.[4] Since the c-axis thermal expansion is mainly coupled to the thermal energy of these longitudinal modes, a one-dimensional quasiharmonic analysis is expected to yield adequate results. Also, we were interested in searching for any a- or c-axis thermal expansion anomalies, which could be related to alkali order-disorder or stacking phase transitions.

In the past Billaud and Hérold[5] have determined the c-axis thermal expansion of stage-1 AGIC's in the temperature range of 25 °C to 155 °C. Bottomley et al.[6] have measured the stage dependence of the thermal expansion of some acceptor compounds, showing a trend to smaller c-axis thermal expansion coefficients with increasing stage number n. They also reported a λ-type anomaly in the thermal expansion of nitrate-graphite compounds at 253 K, which is related to an in-plane order-disorder transition in the NO_3 groups.[7] Recently, room-temperature thermal expansion data of LiC_6 have been reported by Rossat-Mignod et al.[8] A first report of some of our results has been given elsewhere.[9]

In the following we present the first systematic study of the dependence of the c-axis and a-axis thermal expansion of AGIC's on both the intercalation species (K,Rb,Cs) and the stage n of the compound. We have chosen x-ray Bragg-scattering techniques to determine lattice parameter changes instead of optical or capacitive methods, because the latter are complicated by the necessity of rather large samples and/or by the possibility of surface
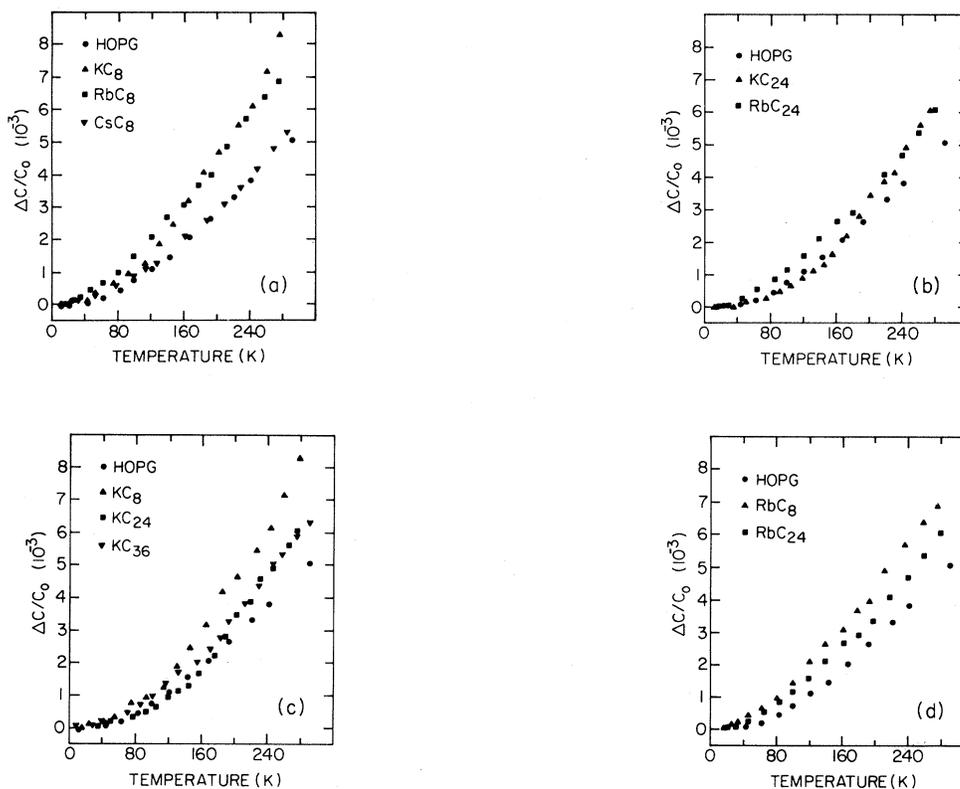
FIG. 1. c-axis thermal expansion of graphite and alkali-metal—graphite intercalation compounds: (a) thermal expansion of stage-1 compounds, (b) of stage-2 compounds, (c) of stage-1, -2, and -3 potassium compounds, and (d) of stage-1 and -2 rubidium compounds.

layer exfoliation. The accuracy of lattice parameter determinations, on the other hand, depends largely on the scattering geometry chosen and the diffraction angle used, and in respect to AGIC's has its limits too. However, under the circumstances given, the x-ray techniques applied here are possibly the best method to study the thermal expansion of AGIC's.

II. EXPERIMENTAL

Grade-ZYB highly orientated pyrolytic graphite (HOPG) from Union Carbide Corporation was used as the pristine graphite material throughout. This material is characterized by a well-defined c-axis alignment [mosaic FWHM$\simeq$0.6° (full width at half maximum)], and a random a-axis orientation within the basal plane. Typical dimensions for the graphite samples were $0.5\times0.2\times0.05$ cm^3. The usual two-bulb method[10] was used to intercalate the pristine HOPG samples with alkali metal (99.9%). After intercalation to the desired stage, the samples were sealed off in a glass holder and inserted into a

closed-cycle ^{4}He refrigerator. The homogeneity of the samples was confirmed by $(00l)$ scans. A calibrated Ge diode, placed near the sample, was used for the temperature measurements over the entire temperature range from 11 to 290 K.

The c-axis measurements were carried out using a Picker FACS I x-ray system with Mo$K\alpha$ radiation, point focus, and a graphite monochromator in the incident beam. Radial θ:2θ scans were taken in reflection geometry and recorded on a strip-chart recorder. Since the angular resolution increases with the Bragg angle θ, back-scattering geometry would have been preferable. However, the rapid decrease of intensity with increasing scattering angle imposes limitations on the order of the Bragg reflection that can be studied with acceptable accuracy. Therefore, the c-axis repeat distances were measured typically at the (008) to (0010) reflections. Only in the case of KC$_{24}$ were we succesful in recording the (0021) reflection with significantly higher resolution.

The a-axis measurements were taken in transmission geometry at (110) or (220) Bragg reflections. Here, the h,k,l Miller indices refer to the graphite

TABLE I. Low-temperature a- and c-axis parameters of AGIC's measured at about 11.0 K.

Compound	a_0 (Å)	C_0 (Å)
HOPG	2.4583	3.3299
KC_8	2.4898	5.2718
KC_{24}	2.4709	8.6698
KC_{36}		12.0946
RbC_8		5.6102
RbC_{24}		8.9753
CsC_8		5.9137

sublattice and the shortest repeat distance in the c-axis direction, disregarding the actual stacking sequence of the compound. For the transmission scattering geometry the resolution obtained by the graphite monochromator was not sufficient. Therefore, we replaced the graphite monochromator by a flat Si(111) single crystal in the incident beam.

Precise absolute lattice parameters were not the object of this experiment and are not needed for the determination of the thermal expansion. However, the typical accuracy for the percentage expansion ($\Delta d/d$) measured at, e.g., a (009) Bragg reflection is about 3×10^{-4}. All data were taken in heating and cooling cycles, and at least two runs were carried out for each sample to check the reproducibility. The data presented are in most cases averaged values from different runs.

III. RESULTS

In Fig. 1(a) the c-axis percentage expansions ($\Delta C/C_0$) of the stage-1 compounds KC_8, RbC_8, and CsC_8 are shown. The lattice parameter C_0 was determined at the lowest measured temperature (see Table I for a complete listing of the C_0 lattice parameters). In Fig. 2(a) the temperature dependence of the thermal expansion coefficients ($\alpha_\perp$) of the same compounds are shown. The coefficients have been obtained by smoothing the experimental data with a cubic spline function and subsequent differentiating with respect to the temperature. In both figures [1(a) and 2(a)] results from measurements at pristine HOPG are included for comparison. The intercalation process is seen to dramatically alter the thermal expansion of stage-1 compounds, which is best illustrated by the 150% increase of the KC_8's $\alpha_\perp$ room-temperature value as compared with HOPG. As the intercalant alkali metals are changed from K to Rb and Cs, the room-temperature values of $\alpha_\perp$ show a systematic decrease [see Table II and Fig. 2(a)]. This observation agrees well with the room-temperature values reported by Billaud and Hérold.[5] Since the 2×2 in-plane alkali-metal structure[11] and the charge
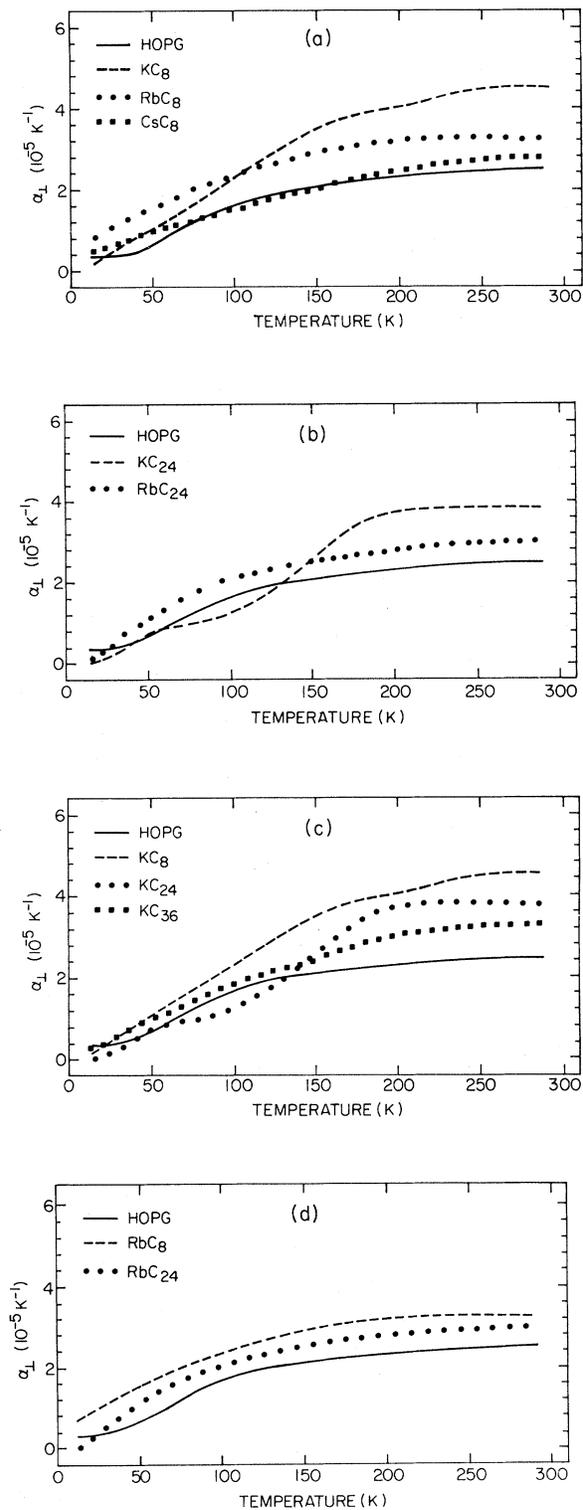
FIG. 2. c-axis thermal expansion coefficients of graphite intercalation compounds. The sequence of the figures is the same as in Fig. 1.

TABLE II. Thermal expansion coefficients for the a axis $(\alpha_{\parallel})$ and c axis $(\alpha_{\perp})$ of graphite and AGIC's. Numbers in parentheses are taken from the literature.

Compound	$-\alpha_{\parallel}$ $(10^{-5}$ $K^{-1})$		Temperature range (K)	$\alpha_{\perp}$ $(10^{-5}$ $K^{-1})$	Temperature range (K)
HOPG	0.20	$(0.127)^{a}$	200—280	$2.4 \pm 0.4 (2.72)^{a}$	200—300
KC_8	0.40		170—285	$4.5 \pm 0.8 (4.3 \pm 0.6)^{b}$	250—300
KC_{24}	0.40		165—280	3.6 ± 0.4	250—300
KC_{36}				3.0 ± 0.6	230—300
RbC_8				$3.0 \pm 0.7 (3.0 \pm 0.5)^{b}$	250—300
RbC_{24}				3.3 ± 0.5	240—300
CsC_8				$2.8 \pm 0.6 (2.5 \pm 0.4)^{b}$	240—300

[a]Reference 2.
[b]Reference 5.

transfer[12] is the same for all three compounds, this result clearly indicates a strong alkali species dependence of the c-axis thermal expansion. The room-temperature value of $\alpha_{\perp} = 6.5 \times 10^{-5}/K$ for stage-1 LiC_6 (Ref. 8) confirms this trend, although the latter compound is different from the other three stage-1 compounds as the in-plane concentration and charge transfer is concerned.

Figures 1(b) and 2(b) show, respectively, the thermal expansion results of the stage-2 compounds KC_{24} and RbC_{24}. Again, the room-temperature $\alpha_{\perp}$ values demonstrate a distinct mass dependence. Both compounds (KC_{24} and RbC_{24}) have been reported to undergo alkali-metal in-plane order-disorder phase transitions at 123 (Refs. 13 and 14) and 165 K,[15,16] respectively, and stacking order changes at 98 (Ref. 13) and 106 K,[16] respectively. The upper transitions show all signs of second-order phase transitions,[14,17] while the lower phase transitions are clearly of first order. In our thermal expansion data we could not find an indication of anomalies at these temperatures, which could be related to the reported phase transitions. The specific-heat data of RbC_{24} (Ref. 18) show only very small anomalies of about 4% around the temperatures 106 and 165 K. Using the Grüneisen relation of Eq. (5), below we estimate an effect for the thermal expansion coefficient of about the same magnitude, which falls within the error bars of our experimental resolution.

The smoothed thermal expansion coefficient $\alpha_{\perp}$ KC_{24} shows much more structure than those for any of the other compounds. The reason for this behavior is not quite clear yet. However, it may be speculated that it is related to the unusually large anharmonicity observed for the acoustic branch of the transverse [100] phonon modes in KC_{24}.[19] This point certainly needs further exploration in future studies.

In Figs. 1(c) and 2(c) the c-axis thermal expan-

sions and coefficients, respectively, are shown for the first three stages of potassium graphite intercalation compounds and compared with the results of pristine HOPG. Similarly, Figs. 1(d) and 2(d) show the thermal expansion of stage-1 and -2 rubidium graphite compounds along with pristine HOPG results. At room temperature, the thermal expansion coefficients are largest for the stage-1 compounds and decrease to approach the value for pristine HOPG as the stage number is increased. This result is not completely unexpected, since an increase in stage number increases the number of interior graphite planes and decreases the relative importance of the alkali-metal—graphite interplanar interaction.

In Fig. 3 are shown the results of the a-axis percentage expansion measurements for HOPG. The a_0 parameters are listed in Table I; note that these parameters confirm the observation first made by Nixon and Parry[20] that the graphite in-plane lattice parameter (or C—C bond length) decreases with the stage number n. Like in pristine graphite, the intercalated samples exhibit a negative a-axis thermal expansion over the entire measured temperature range of 10—290 K. At room temperature, the in-plane thermal expansion coefficients $(\alpha_{\parallel})$ of both KC_8 and KC_{24} are approximately twice as large as for HOPG (see Table II). By taking the ratio of the c-axis to the a-axis thermal expansion coefficients, $\alpha_{\perp}/\alpha_{\parallel}$, the anisotropy is seen not to change dramatically upon intercalation with alkali atoms (see Table III).
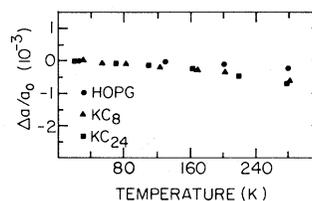
FIG. 3. a-axis thermal expansion of HOPG, KC_8, and KC_{24}.

TABLE III. Anisotropy $(\alpha_\perp/\alpha_{||})$ of potassium GIC's at room temperature.

Compound	$\dfrac{\alpha_\perp}{|\alpha_{||}|}$	Temperature
HOPG	11	200—280
KC_8	11	250—285
KC_{24}	9	250—280

Again, we have not observed any anomaly in the a-axis thermal expansion of KC_{24} which could be related to the alkali-atom order-disorder transition or changes in the stacking sequence.

In the case of KC_8 we also recorded carefully the profile of the (110) graphite reflection, which overlaps with the (220) potassium superstructure reflection. Since the pure potassium metal thermal expansion is large and positive,[21] while the graphite in-plane expansion is negative, it is not unreasonable to expect a discommensuration of both sublattices to develop at a certain temperature. This should affect at least the profile of the (110) reflection. However, in the temperature region considered here, we could not see such an effect.

IV. DISCUSSION

The thermal expansion is often analyzed in terms of a quasiharmonic approximation, in which the lattice anharmonicity gives rise to a frequency change of the phonon modes.[22] In this model the volume thermal expansion $\Delta V/V_0$ can be written in the simplified manner[23]:

$$\frac{\Delta V}{V}(T)=\gamma B^{-1}E_{\text{therm}}(T) \ . \tag{1}$$

Here, B is the bulk modulus and γ is the Grüneisen parameter, defined by

$$\gamma=-\frac{V}{\omega}\frac{\partial \omega}{\partial V} \ , \tag{2}$$

where ω is the frequency of the phonon mode. The thermal energy is obtained by integrating over the phonon density of states $g(\omega)$:

$$E_{\text{therm}}= \int g(\omega)\hbar\omega[n(\omega,T)+\tfrac{1}{2}]d\omega \ . \tag{3}$$

Electronic excitations also contribute to the thermal expansion. However, this effect becomes noticeable only at very low temperatures (below 10 K) and will therefore be neglected in the following discussion.

For crystals with axial symmetry, one finds for the Grüneisen parameters parallel $(\gamma_{||})$ and normal $(\gamma_\perp)$ to the planes[24]:

$$\gamma_{||}=\frac{V}{C_t}[(C_{11}^s+C_{12}^s)\alpha_{||}+C_{13}^s\alpha_\perp] \ ,$$

$$\gamma_\perp=\frac{V}{C_t}[2C_{13}^s\alpha_{||}+C_{33}\alpha_\perp] \ . \tag{4}$$

C_t is the specific heat at constant stress, C_{ij}^s are adiabatic elastic constants, and $\alpha_{||},\alpha_\perp$ are the thermal expansion coefficients in and out of the planes, respectively.

We could not apply the formulas in Eq. (4) for the analysis of the thermal expansion, because the information on the specific heats and/or elastic constants of AGIC's is rather fragmentary, and a comparison of the Grüneisen parameters would not have been possible. Therefore, we have chosen another approach: The c-axis thermal expansion of graphite is linked to the thermal vibration of atoms with polarizations normal to the layers. These are mainly the low-frequency longitudinal [001] and transverse [100] phonon modes. The higher modes are separated from the lower ones by a large frequency gap and can therefore be neglected.[25] It has been shown recently that the longitudinal [001] modes are strongly affected by intercalation. The interplanar coupling constants are changed, and frequency gaps occur at the center and boundary of the Brillouin zones, creating new maxima in the phonon density of states. According to Eq. (1) there are, in principle, two effects which could account for the increased c-axis thermal expansion of AGIC's as compared to pristine graphite: Either the anharmonicity of the interplanar interaction is altered $(\gamma_\perp)$, or the changed phonon density of states yields the major contribution.

In general, both processes are superimposed upon each other, and thus a method must be found to decouple them. Therefore, we have analyzed the c-axis thermal expansions in terms of a one-dimensional quasiharmonic approximation, assuming that the $\gamma_\perp$ for the longitudinal [001] modes is much larger than for the transverse [100] modes. The c-axis thermal expansion is then given by

$$\frac{\Delta C}{C_0}=\frac{\gamma_\perp}{C_{33}V_C}E_{\text{therm}}(T) \ , \tag{5}$$

and the thermal energy is

$$E_{\text{therm}}(T)=\frac{C_0}{2\pi} \int \left|\frac{dK}{d\omega}\right|\hbar\omega \coth\left|\frac{\hbar\omega}{2k_BT}\right|d\omega \ . \tag{6}$$

The elastic constant C_{33} for each compound has been taken from Ref. 4, k_B is the Boltzmann constant, and V_c is the unit cell volume of the linear chain, defined by
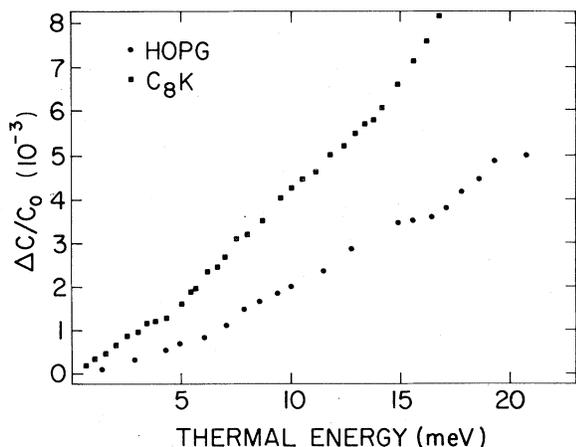
FIG. 4. c-axis thermal expansion of HOPG and KC_8 plotted as a function of the thermal energy, computed from the longitudinal [001] phonon dispersion.

$$V_c = \frac{\sqrt{3}}{4} a^2 I_c^n \ . \tag{7}$$

Here a is the graphite basal plane lattice parameter and I_c^n is the c-axis layer repeat distance in a stage-n compound. Since the longitudinal [001] phonon dispersion curves are known from neutron spectroscopy results[4] for all compounds of interest here, the thermal energy [Eq. (6)] can be calculated for each compound by numerically integrating over the

TABLE IV. Grüneisen parameters for graphite and alkali-metal—graphite intercalation compounds.

Compound	Temperature range	$\gamma_\perp$
HOPG	10—105	0.31
	120—300	0.51
KC_8	10—105	0.68
	125—220	1.04
	240—300	1.64
KC_{24}	10—150	0.38
	160—300	0.93
KC_{36}	10—70	0.30
	90—170	0.47
	190—300	0.70
RbC_8	10—70	0.72
	90—190	0.83
	210—300	0.97
RbC_{24}	10—180	0.33
	200—300	0.46
CsC_8	10—115	0.51
	130—210	0.68
	230—300	0.91

respective phonon branches. By plotting the calculated thermal energy against the measured c-axis thermal expansion $(\Delta C/C_0)$, the Grüneisen parameters can be gleaned. Figure 4 shows a typical result for the above procedure for KC_8 and HOPG. In Table IV, the Grüneisen parameters gained by the above procedure are listed. The anharmonicity of the vibrational interaction in the c axis is seen to be greatly influenced by the intercalation process. Stage-1 compounds show an increased $\gamma_\perp$ at low temperatures which becomes even larger at room temperature. Stage 2 and stage 3 show similar results following the general trend $\gamma_{\perp,1} > \gamma_{\perp,2} > \gamma_{\perp,3} > \gamma_{\perp,HOPG}$. Therefore, the large increase in the thermal expansion observed is dominantly due to an increase in the anharmonicity of the interlayer interaction, rather than to changes in the thermal energy. In fact, we noticed that the thermal energies calculated from the longitudinal [001] branches differ only little between graphite and the different compounds over the temperature range considered here. This result, at first sight surprising, is caused by a partial compensation between flat parts in the phonon branches at higher energies with a steeper slope of the acoustical branch at lower energies.

Since we have also observed a dependence on alkali species and stage, we believe that the increased c-axis thermal expansion is caused mainly by a strong and rather anharmonic alkali-metal—graphite interplanar interaction.

The large a-axis thermal expansion of AGIC's is somewhat unexpected. Assuming that the C—C bond length does not change drastically with temperature, this result implies that the vibrational amplitude of the transverse [100] or layer bending modes increase in the intercalated samples, which in turn would result in an effective shrinkage of the in-plane distances upon heating. This explanation would be consistent with the observation of an overall softening of the bending modulus in AGIC's as compared to pristine graphite.[19]

V. SUMMARY

We have measured and analyzed the a-and c-axis thermal expansion of highly oriented pyrolytic graphite and of alkali-metal—graphite intercalation compounds. By varying the intercalant species (K, Rb, and Cs) for a fixed stage we have observed a strong mass dependence of the c-axis thermal expansion, which decreases from the lighter to the heavier atoms. Keeping the intercalant species constant, the thermal expansion is largest for stage-1 compounds and decreases with increasing stage number to approach the value for pristine graphite. We have analyzed the c-axis data by a one-dimensional

quasiharmonic approximation in which the thermal energy has been calculated from the longitudinal [001] phonon branches of each compound. The derived Grüneisen parameters show the same trend as the thermal expansion, being larger for light intercalants and low stages. This behavior indicates that the increased c-axis thermal expansion is predominantly due to a strong and anharmonic alkali-metal—graphite interplanar interaction. The a-axis thermal expansion of KC_8 and KC_{24} is negative in the temperature range from 10 to 300 K, with a room-temperature coefficient about twice as large as for pristine graphite.

ACKNOWLEDGMENTS

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