THERMAL EXPANSION OF ALKALI-GRAFITE INTERCALATION COMPOUNDS

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Abstract. The c-axis thermal expansion of several alkali-graphite intercalation compounds has been measured by means of x-ray scattering between 15 and 300 K. The thermal expansion depends strongly on the stage of the compound and is largest for C\textsubscript{6}M (M=K,Rb,Cs) compounds. The data have been analyzed in terms of a one-dimensional quasi-harmonic approximation, which yields Grüneisen parameters two or three times as large as for pristine graphite.

1. Introduction. - There is an intrinsic interest in the study of the thermal expansion (TE) of graphite and graphite intercalation compounds, because of their high anisotropy and unusually large anharmonic properties. The c-axis TE of pristine graphite is large (2.8 x 10\textsuperscript{-5}/K) and positive, while the a-axis TE is very small and slightly negative at room temperature.\textsuperscript{1} The vibrational and thermal properties of graphite can artificially be changed by inserting monatomic layers of alkali atoms between the Van der Waals gap of graphite planes.\textsuperscript{2} In these alkali-graphite intercalation compounds (AGIC's) the graphite and alkali planes form a regular stack along the hexagonal c-axis. In the following we report on a systematic study of the c-axis TE of AGIC's in dependence of the stage n of the compound (n designates the number of graphite planes between two intercalated planes) and the alkali atoms chosen by means of x-ray Bragg-scattering.

2. Experimental. - Highly oriented pyrolytic graphite (HOPG) was intercalated with alkali atoms by the two-bulb method in the usual manner.\textsuperscript{3} The homogeneity and stage of the compound was determined by (00l) scans. The TE was measured between 15 and 300 K during heating and cooling cycles with MoK\textsubscript{α} radiation. A more detailed description of the experimental set up will be given elsewhere.

3. Results. - In Fig. 1a the c-axis TE of stage 1 K, Rb, and Cs GIC's is compared with pristine graphite, and in Fig. 1b the comparison is made with stage 2 K and Rb compounds. In Fig. 1c the c-axis TE's of stages 1 through 3 of K GIC's are plotted. In each case the data are normalized to the lattice constant c\textsubscript{0}, taken at the lowest measured temperature. In all cases the TE shows a characteristic zero slope at low temperatures, due to the thermal occupation number. Stage 1 compounds exhibit the largest TE, while the TE's of higher stage compounds approach the value of pristine graphite. This behavior is not unexpected, since the frequency spectrum of the higher stage compounds is dominated by the vibration of the
interior graphite planes.

Fig. 1: Thermal expansion of alkali-graphite intercalation compounds, (a) of stage 1 K, Rb, Cs compounds, (b) of stage 2 K, and Rb. In (c) different stages of K compounds are compared.

4. Discussion. - The c-axis thermal expansion is linked to the thermal vibration of atoms with polarization in the c-direction. These are mainly the low frequency [001]L modes. The higher modes are separated from the lower by a large frequency gap and can therefore be neglected. It has been shown recently that the [001]L modes are strongly influenced 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 density of states. There are in principal two possible reasons for an increased TE of AGIC's as compared to pristine graphite: either the phonon density of states increased and/or the anharmonicity of the vibrational potential is enhanced. To elucidate these possibilities, the TE's have been analyzed in terms of a 1-D quasi-harmonic approximation, in which the relative change of the c-axis is given by:

\[ \frac{\Delta C}{C_0} = \frac{\gamma_c}{C_{33}} V_c E_{\text{therm}}, \quad \gamma_c = - \frac{3 \ln(\omega)}{3 \ln(\Delta C/C_0)} \]

and the thermal energy is:

\[ E_{\text{therm}} = \frac{c_o}{2\pi} \int \frac{dk}{d\omega} \frac{k_B \omega}{\omega - \omega} \frac{\omega}{2k_B T} d\omega. \]

Here \( \gamma_c \) is the mode Gr"uneisen parameter, the elastic constants \( C_{33} \) for each compound have been taken from Ref. 5, \( V_c \) is the volume of a unit cell, \( \omega \) is the lattice vibrational frequency, and \( k_B \) is the Boltzmann constant. The thermal energy has been determined by numerical integration over the measured [001]L phonon dispersions.
In Fig. 2 the TE is plotted against the thermal energy for the compound C\textsubscript{8}K. From Table 1 parameters gained in this way for K compounds are listed and compared with HOPG. The Grüneisen parameter of pristine graphite is in good agreement with published data.\textsuperscript{7} The anharmonicity of the lattice vibrations in \textit{c}-direction seems severely influenced by the intercalation process: stage 1 compounds show a considerably higher $\gamma_\text{c}$ at low temperatures, which even increases at higher temperatures. Also, stage 2 and 3 compounds exhibit increased Grüneisen parameters. Therefore, we believe that the dominant effect for the large TE of A\textit{GIC}'s is an increased anharmonicity of the lattice vibrations, rather than the higher density of states in the frequency region considered here.

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