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A. Schirmer [a e], J. E. Fischer [b], P. Heitjans [a], H. J. Kim [c f], A. Magerl [c], D. Vaknin [b g] & H. Zabel [d]

[a] Institut für Physikalische Chemie, Universität Hannover Callinstr, 3-3a, 30167, Hannover 1, Germany

[b] Materials Science Department, University of Pennsylvania, 3231 Walnut St, Philadelphia, PA, 19104, USA

[c] Institut Laue Langevin, 156X, 38042, Grenoble, France

[d] Experimentalphysik IV, Ruhr-Universität Bochum, Postfach 102148, 44721, Bochum, Germany

[e] Institut für Festkörperforschung, Forschungszentrum Jülich, 52425, Jülich, Germany

[f] Hallym University, Chanchun, South Korea

[g] Physics Department, Ames Laboratory USDOE, ISU, Ames Iowa, 50011, USA

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IN-PLANE PHONON DENSITY OF STATES OF Li-GRAPHITE INTERCALATION COMPOUNDS

A. SCHIRMER[a1], J.E. FISCHER[b], P. HEITJANS[a], H.J. KIM[c2]
A. MAGERL[c], D. VAKNIN[b3], H. ZABEL[d]

[a] Institut für Physikalische Chemie, Universität Hannover
Callinstr. 3-3a, 30167 Hannover 1, Germany

[b] Materials Science Department, University of Pennsylvania,
3231 Walnut St, Philadelphia PA 19104, USA

[c] Institut Laue Langevin, 156X, 38042 Grenoble, France

[d] Experimentalphysik IV, Ruhr-Universität Bochum,
Postfach 102148, 44721 Bochum, Germany

Abstract The in-plane phonon densities of states of Li-graphite intercalation compounds of stage-1 and stage-2 are obtained from neutron time-of-flight spectra. For the stage-2 the ordered compound LiC_{12} which has the same in-plane structure as the stage-1 compound LiC_6 as well as the dilute compound LiC_{16} which only reveals short range order were studied. The temperature in the measurements was extended above expected phase transitions for both stages and the density of states is analysed in terms of the effective temperatures $T_{\|}$ for the in-plane vibrational energies. $T_{\|}$ shows characteristic changes at the thermodynamic temperatures of the phase tansitions. Comparison of the $T_{\|}$ values shows similar in-plane dynamics of all Li-compounds at the highest temperatures.

INTRODUCTION

The lattice dynamics of alkali-graphite intercalation compounds (GICs) is associated with interlayer and intralayer modes. The first are predominantly high frequency modes, whereas the intralayer modes comprise low frequency layer breathing and shear modes propagating in the basal plane. In extensive studies on GICs with different alkalis as well as on different stages inelastic neutron scattering measurements have contributed detailed information (for a review see [1]).

For the Li-graphite system, however, neutron scattering experiments have been performed only on the stage-1 compound LiC_6. The existence of two distinct stage-2

[1]also at: Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany
[2]present address: Hallym University, Chanchun, South Korea
[3]present address: Physics Department, Ames Laboratory USDOE, ISU, Ames Iowa 50011, USA

phases which are stable in different but overlapping temperature ranges is a unique feature of the Li-GIC system: (*i*) LiC_{12} is an ordered stoichiometric compound with the same $\sqrt{3} \times \sqrt{3}$ in-plane superlattice as LiC_6 and it transforms above about 500K to stage-1 with no long-range in-plane order. (*ii*) The dilute non-stoichiometric stage-2 phase, which we assign LiC_{16}, has no long-range order already at ambient temperature.

For the stage-2 GICs the [00*l*]-phonon dispersion revealed dramatic differences in the elastic properties between ordered and dilute compounds which arise from different in-plane densities as well as from different interlayer interactions [2] Here the in-plane phonon density of states (DOS) of both stage-2 compounds and LiC_6 are obtained from the analysis of incoherent inelastic neutron scattering spectra measured with neutron time-of-flight (TOF) techniques. The measurements on both stages are extended from ambient temperatures to higher ones.

EXPERIMENTAL

The stage-1 compounds were prepared at the Argonne National Laboratory, the stage-2 compounds at the University of Pennsylvania. The samples had been used in former TOF measurements of the quasielastic line broadening due to Li diffusion [3,4]. For the stage-1 sample an admixture of less than 3% [5] of a stage-2 phase and for the stage-2 samples a stage-1 admixture below 1% was estimated from elastic neutron scattering measurements. The mosaic spread was for all samples about 7°.

The measurements were done at the Institute Laue Langevin, Grenoble, with the time-of-flight spectrometers IN5 for LiC_6 and IN6 for the stage-2 compounds. The neutron wavelength was 7.5$\AA$ for IN5 and 5.1$\AA$ for IN6. The samples were mounted such that the scattering plane was perpendicular to the c-axis. The HOPG-based samples are thus regarded as two-dimensional polycrystals and a uniform sampling over all intercalate modes with phonon wave vectors and atomic displacements in the basal plane are measured. In both spectrometers the entire accessible range of scattered neutron wave vectors Q was used. The Q range was above in-plane zone boundaries of ordered intercalate phases as well as above $2\pi/d_{NN}$ of disordered phases, where d_{NN} denotes the nearest-neighbor distance in the plane, so that the phonon density of states of the entire Brillouin zone was accessible.

The temperature range in the LiC_6 measurements was extended up to 720K, i.e. above the in-plane melting observed at about 700K. Inspection of the elastic line already revealed a large broadening due to an enhancement of the diffusivity in the molten phase with respect to the ordered one [3]. The measurements of the stage-2 compounds were extended up to 650K covering thus temperatures above an expected order/disorder transition at about 500K.

From the TOF spectra the scattering function is obtained by the usual way of correcting for background and detector sensitivity. The phonon density of states $Z(\nu)$ is related to the symmetrized incoherent scattering function $S(Q,\nu)$ via

$$S(Q,\nu) = \frac{h}{2M} Q^2 e^{-2W} \frac{Z(\nu)}{\nu} \left[2 \sinh \left(\frac{2h\nu}{kT} \right) \right]^{-1} . \qquad (1)$$

Here e^{-2W} is the Debye-Waller factor and M the mass of the intercalate atom. By introducing the dimensionless variables $\alpha = hQ^2/2MkT$ and $\beta = h\nu/kT$ the DOS is calculated by transforming $S(Q,\nu)$ into $\tilde{S}(\alpha,\beta)$ and extrapolating $\alpha \to 0$

$$Z(\nu) = 2\beta \sinh(\frac{\beta}{2}) \lim_{\alpha\to 0}\left[\ln \frac{\tilde{S}(\alpha,\beta)}{\alpha}\right]. \quad (2)$$

We note that (2) does not account for multiphonon scattering. But since multiphonon scattering results in a featureless function of ν, $Z(\nu)$ derived from the spectra via eqn. (2) should not be grossly in error. Furthermore multiphonon scattering should lead to an upturn of the right hand side of (2) for finite values of α and small energy transfers which was not observed in the data evaluation. In the data reduction and extrapolation procedure no normalisation to the number of scatterers was performed.

RESULTS AND DISCUSSION

The discussion of the phonon density of states will be limited to the range below 10THz, where features corresponding to that of earlier measurements on stage-1 GICs of heavy alkalis [7] are observed. Figure 1 shows $Z(\nu)$ for LiC_6 at different temperatures. The DOS of the stage-2 compounds is shown in figure 2. For the ordered compounds of both stages $Z(\nu)$ shows two peaks at the lowest temperature of the measurements. For LiC_6 the intensity of $Z(\nu)$ decreases drastically and becomes featureless with rising temperature. For the ordered stage-2 compound LiC_{12} only minor changes of $Z(\nu)$ with rising T were observed and the DOS of LiC_{16} remains almost unchanged at higher temperatures.

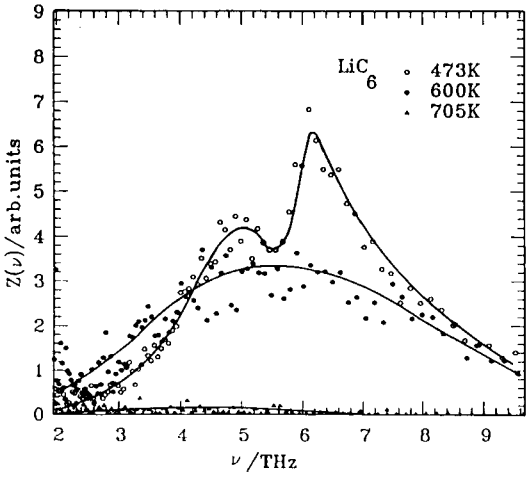

FIGURE 1: In-plane phonon density of states $Z(\nu)$ of LiC_6 for different temperatures. The lines are guides to the eye.

In the study of the heavy alkali-GICs similar two peak structures in $Z(\nu)$ were found, but the separations of the peaks and the minimum in between was more pro-

nounced. The DOS spectra of the heavy alkali GICs can be described by interactions between intercalate metal atoms themselves (M_x-M_x interactions) and interactions between the metal atoms and the graphite planes (M_x-C interactions) [6]. With a short range M_x-C coupling and long range Coulomb forces between M_x^+ ions a satisfactory description with only one adjustable parameter, ν_0, was obtained which describes the M_x-C coupling. Then $M_x \nu_0^2$ is the curvature of the potential due to bounding graphitic layers felt by the alkali atoms and ν_0 is found to be slightly below the frequency of the lower-energy peak. The higher-energy peak would in the absence of M_x-C coupling occur close to the ion-plasma frequency $\nu_p = e/\sqrt{\pi M_x V}$, where V is the volume per M_x ion. Taking into account the M_x-C coupling the higher-energy peak is shifted to $(\nu_0^2 + \nu_p^2)^{1/2}$. In LiC_6 the in plane phonon density of states exhibits a high-energy peak at about 6THz. This is substantially below the ion-plasma frequency which is about 10THz. LiC_6 thus contrasts the other alkali GICs and for the description of $Z(\nu)$ modifications of the Coulombic force model have to be considered here. A factor which did not play any role in the heavy alkali GICs is the screening contribution to the motion of the ion cores. In the DOS of alkali metals the maximum phonon frequency is scaled down from ν_p to about 0.5 ν_p due to conduction electron screening which might play a major role in the Li GICs.

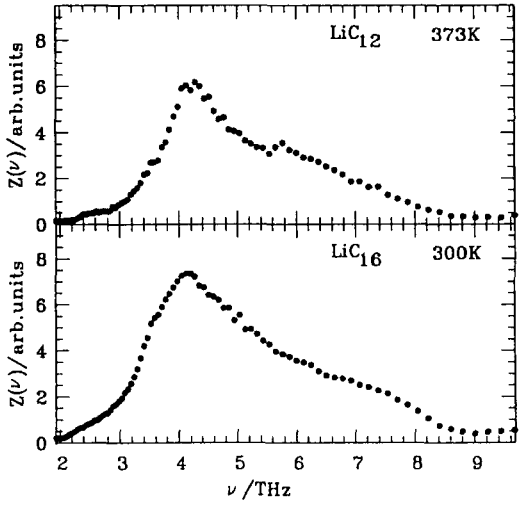

FIGURE 2: In-plane phonon density of states $Z(\nu)$ of the dilute non long range ordered stage-2 compound LiC_{16} and the ordered stage-2 compound LiC_{12}.

For the stage-2 compound LiC_{12} the peaks of $Z(\nu)$ are slightly shifted to lower energies with respect to those of the stage-1 compound (figure 2). A corresponding behaviour is found in the heavy alkali GICs. The DOS of LiC_{16} appears more featureless than that of LiC_{12} (figure 2). Figure 3 shows the DOS of LiC_{12} also for higher temperatures.

In order to discuss quantitatively the small changes in the density of states of the

stage-2 compounds with rising T we adopt the characterization of the DOS used by Moreh *et al* [7]. The vibrational energies of the alkali metal atoms are expressed in terms of effective temperatures $T_{\|}$ and $T_{\perp}$ for elongations parallel and perpendicular to the graphene layers. The temperatures $T_{\|}$ and $T_{\perp}$ differ from the thermodynamic temperature T since they include the zero-point vibrational motion. From the in-plane DOS $Z(\nu)$ the corresponding effective temperature $T_{\|}$ is calculated via

$$kT_{\|} = \frac{\int_0^{\nu_{\|}} Z(\nu)\, h\nu\, a\, d\nu}{\int_0^{\nu_{\|}} Z(\nu)\, d\nu} \tag{3}$$

where $\nu_{\|}$ is the maximum frequency of the in-plane vibrational modes and the factor a is given by

$$a = [\exp(h\nu/kT) - 1]^{-1} + \frac{1}{2} \tag{4}$$

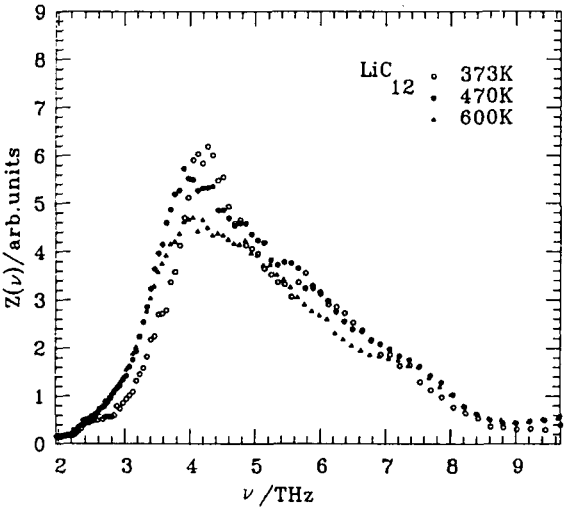

FIGURE 3: $Z(\nu)$ of LiC_{12} for different temperatures

In [7] $T_{\|}$ and $T_{\perp}$, which is given by a formula similar to (3), are calculated for an entire series of heavy alkali GICs of different stages. A linear dependence of $T_{\|}$ on $M_x^{-1/2}$ was observed, where M_x is the mass of the alkali atom. This implies similar spring constants for the description of the in-plane dynamics of the heavy alkali GICs. From the systematics $T_{\|}$ values for stage-1 and stage-2 Li-GICs are predicted as $T_{\|} = 147$K for both stages with no consideration of different in-plane densities of the stage-2 compounds. Evaluation using the measured $Z(\nu)$ in the ν range shown in figure 1 and figure 2, respectively, yields $T_{\|}(LiC_6) = 147$K, $T_{\|}(LiC_{12})$ $= 124$K and $T_{\|}(LiC_{16}) = 120$K. We thus obtain a lower value than predicted for the stage-2 compounds, which might be due to the somewhat poorer systematics being based on less experimental data than for the stage-1 compounds. In both cases the extrapolation involves the factor $M_x^{-1/2}$ which changes more as one goes from the heavy alkalis to Li than within the heavy alkalis themselves, which are the base of the systematics.

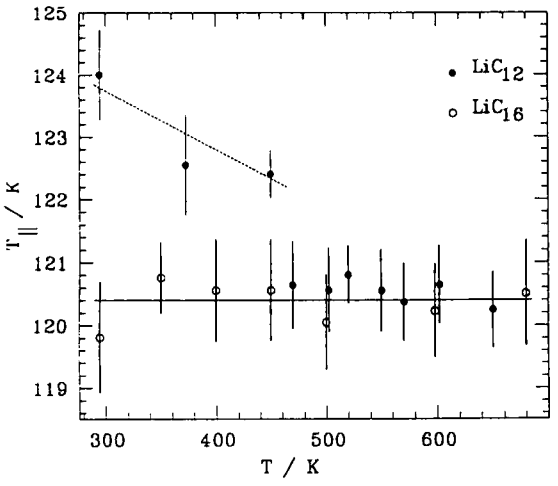

FIGURE 4: The effective temperature $T_{\|}$ as a function of the thermodynamic temperature T for the stage-2 Li-GICs. The solid line is the temperature independent $T_{\|}$ value for LiC_{16} and the high-T value for LiC_{12}, the decrease of $T_{\|}$ of LiC_{12} with increasing T at low temperatures is indicated by the dashed line.

The calculation of $T_{\|}$ was repeated for the $Z(\nu)$ data at higher temperatures. For LiC_6 $T_{\|}$ decreases to about 115K at the highest temperature which was above the expected in-plane melting. For the stage-2 compounds a systematic dependence of $T_{\|}$ on the thermodynamic temperature T is shown in figure 4. For the ordered phase LiC_{12} a slight decrease of $T_{\|}$ with rising T is followed by a step-like reduction at about 470K to the value of $T_{\|}$ found for the dilute stage-2 phase LiC_{16}. For LiC_{16} no T dependence of $T_{\|}$ is observed. We note that the high-T values of all three Li-GICs are similar in spite of the featureless shape of the high-T $Z(\nu)$ of LiC_6. This indicates that the in-plane dynamics in all high-T phases of Li-GICs is governed by the same coupling. Finally we emphasize the distinction between the stage-2 Li GICs and the stage-2 heavy-alkali GICs. In the latter the coexistence of solid and liquid-like dynamical features above the in-plane melting transition being mediated by domain walls was observed [6]. The behaviour of LiC_{12} and LiC_{16} suggests either that the domains are large or that the Li layer is locally commensurate at all temperatures as implied by Kim *et al* [8].

CONCLUSION

The low-energy part of the in-plane phonon densities of states of Li-GICs shows features similar to those in the DOS of heavy alkali GICs. For the stage-1 compound the couplings that described successfully the in-plane dynamics there have to be modified. For the stage-2 compounds downshifts in the peak energies are observed

in a similar way as in the other alkali GICs. The dilute stage-2 compound LiC_{16} exhibits a more featureless $Z(\nu)$ than LiC_{12}. The evaluation of $Z(\nu)$ in terms of effective temperatures $T_{\|}$ for the in-plane vibrational energy of LiC_{12} shows a step function like decrease to $T_{\|}$ of LiC_{16} in the vicinity of the expected order/disorder transition at 500K. The high-temperature value for $T_{\|}$ of LiC_6 being at thermodynamic temperatures above the in-plane melting and those of both stage-2 compounds are approximately the same indicating that the in-plane dynamics then is dominated by the same coupling.

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REFERENCES

[1] H. Zabel in: Graphite Intercalation Compounds, ed. by H. Zabel and S.A. Solin, Springer, Heidelberg, Berlin, New York (1990), p.101

[2] K.C. Woo, W.A. Kamitakahara, D.P. DiVincenzo, D.S. Robson, H. Mertwoy, J.W. Milliken, and J.E. Fischer, Phys. Rev. Lett., 50, 182 (1983)

[3] A. Magerl, H. Zabel, and I.S. Anderson, Phys. Rev. Lett., 55, 222 (1985)

[4] H.J. Kim, A. Magerl, J.E. Fischer, D. Vaknin, P. Heitjans, and A. Schirmer in: Chemical Physics of Intercalation II, NATO ASI Series B 305, ed. by P. Bernier, J.E. Fischer, S. Roth, and S.A. Solin, Plenum, New York (1993), p.355

[5] H. Zabel, A. Magerl, and J.J. Rush, Phys. Rev. B, 27, 3930 (1983)

[6] W.A. Kamitakahara, and H. Zabel, Phys. Rev B, 32, 7817 (1985)

[7] R. Moreh, N. Shnieg, and H. Zabel, Phys. Rev. B, 44, 1311 (1991)

[8] H.J Kim, A. Magerl, J.L. Soubeyroux, and J.E. Fischer, Phys. Rev B, 39, 4670 (1989)