RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 33, NUMBER 2 15 JANUARY 1986

Localized phonons in stage-disordered graphite intercalation compounds

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(Received 11 September 1985)

The effect of stage disorder on [001] L phonons in intercalated graphite is studied. The energies of localized phonons and the phonon density of states as a function of disorder are predicted for stage-4 potassium graphite.

Phonons in one-dimensional disordered atomic chains have been extensively studied theoretically in the past.[1] This is a class of simple models where important ideas such as Anderson localization[2] can be applied. Yet we are not aware of any experimental realization of such models. It is well known that [001] longitudinal phonons in alkali-metal–graphite intercalation compounds[3] (AGIC's) can be thought of as vibrations of a one-dimensional chain of stacked graphite and alkali-metal layers. Stage-ordered samples (here a stage-n compound is an ordered sequence of stage-n units, each consisting of n graphite and one intercalant layers) have been studied experimentally and this simple picture was fully verified.[4,5] At the same time, stage disorder has only recently attracted a great deal of attention.[6,7] Here the disorder is characterized by a random distribution of stage-$(n\pm1)$, -$(n\pm2),\ldots,(n>2)$ units in the stage-n compound. It is the purpose of this work to point out that the stage-disordered AGIC's are a unique realization of the disordered atomic chains. Moreover, this novel type of disorder is interesting in its own right. Therefore we study the localization of phonons in stage disordered GIC's.

The model adopted here is similar to that of Ref. 4. It consists of an array of N stage-n units. Each stage unit consists of one effective intercalant atom of mass M_i and n graphite atoms of mass $M_{\rm C}$. Spring constants between the intercalant and graphite layers are denoted by $\phi_{{\rm C}\text{-}i}$ and between graphite layers by $\phi_{\rm C\text{-}C}$ and are taken to be the same for every stage unit. The classical equation of motion for the atom is

$$M_l\ddot{u}_l(t)=-\sum_{l'}\phi_{l,l'}u_{l'}(t)\ , \tag{1}$$

where M_l and $u_l(t)=u_l\exp(-i\omega t)$ are the mass and displacement of the lth atom and $\phi_{l,l'}$ describes the force constant for atoms l and l'. For the stage-ordered chain with periodic boundary conditions there is one acoustical (A) and n optical ($O1,\ldots,On$) phonon branches. They are shown in Fig. 1 for the values of parameters $n=4$, $M_i=3.25$ amu, $M_{\rm C}=12$ amu, $\phi_{\rm C\text{-}K}=3450$ dyn/cm, and $\phi_{\rm C\text{-}C}=2850$ dyn/cm. The force constants and effective masses are those obtained by Magerl and Zabel[4] for stage-3 potassium graphite, $\rm C_{36}K$, and we expect them to describe realistically stage-4 ($\rm C_{48}K$) compounds as well. We have chosen stage 4 here because stage disorder increases with stage number, and disorder in stage-4 $\rm C_{48}K$ has been observed by x-ray scattering.[7] The disorder is introduced by replacing at random a fraction of stage-4 units by other stage units while keeping the total number of intercalant atoms constant. According to Kirczenow,[6] a fraction of stage-n units in a stage-n_0 compound can well be approximated by a Gaussian,

$$f_{n_0}(n)=\exp\{-[\alpha/2(n-n_0)]^2\}\ , \tag{2}$$

where α contains all information about the system. The fraction $f_{n_0}(n)$ can also be directly measured by x-ray scattering.[7] Here we assume that f is appreciable only for $n=3$ and $n=5$, as is the case in Refs. 6 and 7.

The quantity of interest here is the phonon density of states. For disordered chains composed of two different masses, it is known that infinitesimal gaps occur in the frequency spectrum for certain ranges of the parameters.[8] We will not be concerned with this in our work. The density of

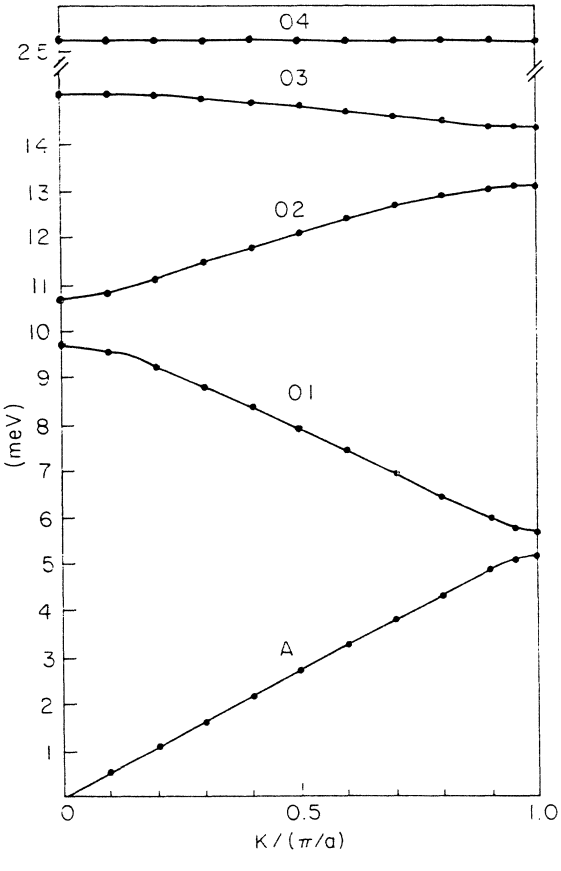

FIG. 1. The dispersion relation for an ordered stage-4 chain. There is one acoustical (A) and four optical (O) branches. a is the stage-4 repeat distance.

states can be computed using a well-known numerical algorithm based on Sturm sequences and discussed in detail by Dean.[9] The method requires fixed-end boundary conditions.[10] It yields very accurately the distribution $G(\omega^2)$ of the eigenvalues of Eq. (1), which is related to the density of states $g(\omega)$ by $g(\omega)=2\omega G(\omega^2)$. We shall use $G(\omega^2)$ as the density of states (DOS) in what follows. The reader is reminded that this is a partial density of states due to $(00l)$ longitudinal phonons only.

Before we turn to the effect of disorder we calculate the energies of localized phonons associated with single stage-3 and stage-5 impurity units. We start with a single impurity unit and then build a chain by adding stage-4 units on both sides of the impurity. At every step a distribution of eigenmodes of the system is calculated and plotted as a function of the chain length in Figs. 2(a) and 2(b). The thick lines give the boundaries of the phonon bands in an infinite ordered stage-4 system and broken lines show the evolution of normal modes of the isolated impurity (we do not show the highest frequency branch in the vicinity of the $O4$ phonon branch because it is not affected by disorder in any interesting way). Note that the energies of every stage-3 mode lie in the stage-4 energy gaps. They do not vary with the increase of the size of the system, giving an approximate localization length of about two stage-4 units. Much of this is true for a stage-5 impurity except for the lowest energy phonon mode denoted by a_5. The energy of this mode lies within the stage-4 acoustical band. This is a resonance mode, an analog of a resonance mode associated with a heavy-atom impurity in a monoatomic chain. On the basis of this analysis we conjecture that for a given stage n_0, stage-$(n<n_0)$ units will generate localized gap modes, while stage-$(n>n_0)$ units will generate both gap and resonance modes, but clearly every case has to be carefully examined before any quantitative conclusion can be drawn. Note that resonance modes which lie within a band are not accessible through the density-of-states calculations. This has been circumvented by the method described above. Table I summarizes the numerical values of the localized phonon energies together with the energies corresponding to the band boundaries.

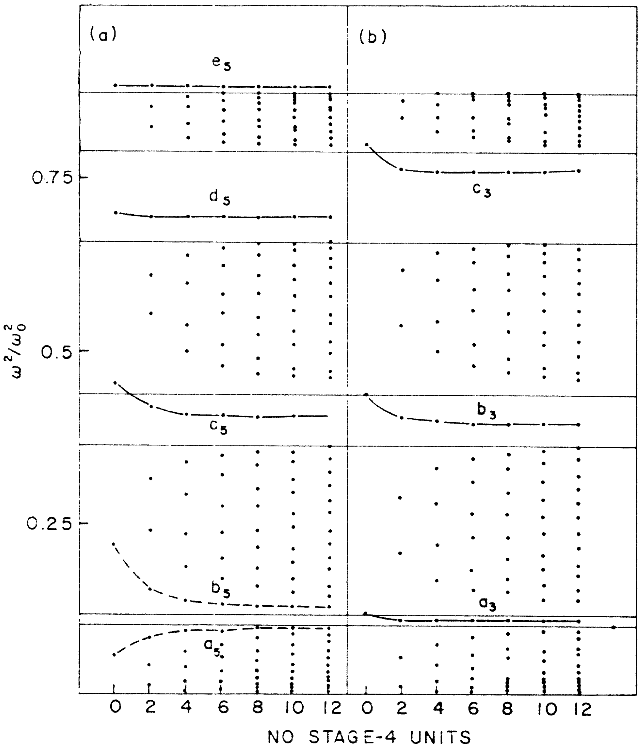

FIG. 2. Distribution of eigenvalues of a chain with a single impurity as a function of host chain (stage-4) length. (a), stage-5 impurity; (b), stage-3 impurity. Solid lines indicate band edges of the pure stage-4 chain. b_5 enters the band gap at longer lengths. $\omega_0=16.15$ meV.

We now turn to the effect of disorder on the $(00l)$ phonon density of states. Figure 3(a) shows the density of states $G(\omega^2)$ for a chain of N stage-4 units ($N=2500$) with single stage-3 and stage-5 impurity units. The density of states is in excellent agreement with the DOS calculated for an infinite system. Gap modes are indicated by the arrows. The modes in the lowest energy gap are not shown here, as they are not distinguishable from the band edges on this scale. Also, the high-energy modes are not shown here, as they are affected little by disorder. Figures 3(b), 3(c), and 3(d) show the evolution of the DOS as a function of the fraction of stage-3 and -5 units $[f_4(3)=f_4(5)=f]$.[11] The effect of small disorder ($f=0.05$) is essentially the increase in intensity of the peaks corresponding to isolated stage-3 and -5 units. Otherwise, the overall structure is essentially that of an ordered chain. As the amount of disorder is increased ($f=0.10$) we observe gradual closing of a low-frequency gap and appearance of many new modes in higher frequency gaps. The structure due to stage-3 and -5 units is clearly visible. For the highest amount of disorder ($f=0.25$) the only structure is due to the high-frequency modes of both stage-3 and -5 units. It is interesting to compare the density of states of a highly disordered sample with the random mixture of potassium and graphite atoms as shown in Fig. 3(e). While there is no essential difference in the low-frequency region, the high-frequency part of the stage-disordered spectrum exhibits more structure due to the high degree of local order. As a consequence the bandwidth is also smaller in case of stage disorder as compared to the random mixture.

In summary, we have discussed for the first time the effect of stage disorder on [001] L phonons in intercalation compounds. The energies of localized phonons and the density of states are calculated as a function of disorder for stage-4 potassium graphite. Our predictions can be verified by the inelastic neutron scattering, and we hope that our work will stimulate such experiments. It would also provide

TABLE I. The energies of localized phonons of stage-3 and -5 units in stage-4 potassium graphite together with phonon band edges.

Lower band edge (meV)	Stage-3 unit (meV)	Stage-5 unit (meV)	Upper band edge (meV)
5.20	5.25	5.62	5.69
9.74	10.11	10.27	10.72
13.11	14.05	13.44	14.36
15.10	25.25	15.19	25.26

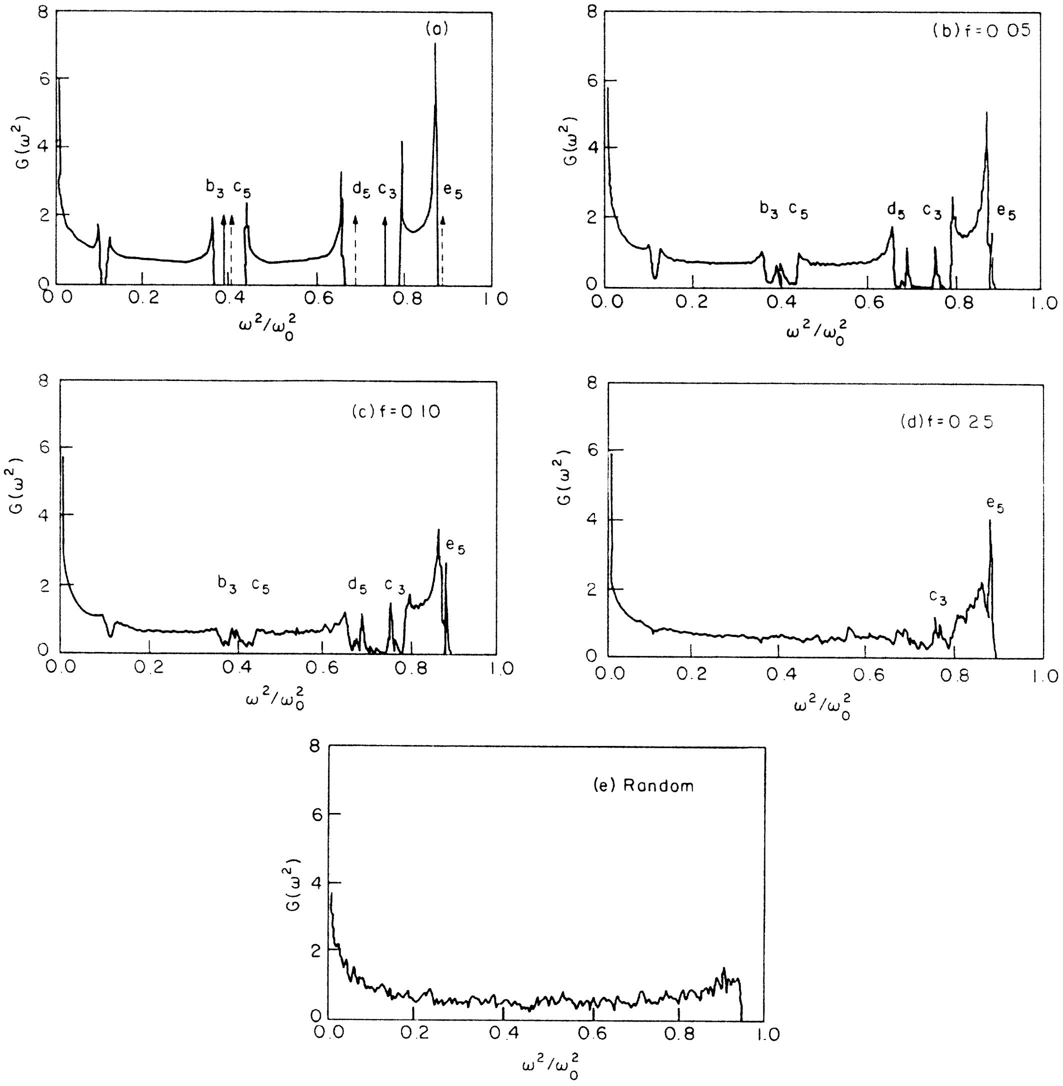

FIG. 3. The density of states of a stage-4 chain with stage-3 and stage-5 impurities. (a), ordered chain with single stage-3 and stage-5 impurity modes indicated; (b), $f = 0.05$; (c), $f = 0.10$; (d), $f = 0.25$; (e), random atomic arrangement. $\omega_0 = 16.15$ meV.

an independent check on the stage disorder distribution function f.

These preliminary results form a necessary step toward the understanding of the effect of stage disorder on infrared and Raman absorption and c-axis thermal conductivity.

The authors wish to thank Professor J. J. Quinn, Professor H. J. Maris, and Professor K. R. Subbaswamy for helpful discussions and careful reading of the manuscript. One of us (P.H.) acknowledges the financial support of the U.S. Army Research Office, Durham, NC.

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[10] Fixed-end boundary conditions reproduce very well analytical results obtained by applying periodic boundary conditions.

[11] Our results pertain to the sample with average density corresponding to that of a stage-4 compound, so $f_4(3) = f_4(5)$. The experiment of Ref. 7 indicates different admixtures of stage-5 and stage-3 units, indicating that the density deviates from that of a stage-4 compound. This may hinder a direct comparison of these results with experiment. The work addressing directly stage distribution of Ref. 7 is in progress.