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Possible existence of Lyddane-Sachs-Teller splitting in graphite intercalation compounds

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Inelastic neutron scattering has been used to probe the Lyddane-Sachs-Teller splitting of phonons with polarization perpendicular to the graphite basal plane in the stage-1 graphite intercalation compound CsC_8. The result of $|\Delta\omega| < 0.15$ meV sets an upper limit on the anisotropy of the plasma frequency in this material. The possibility of a larger splitting in other graphite intercalation compounds is discussed.

Graphite intercalation compounds form a class of layered compounds which are highly anisotropic in both their electronic and lattice dynamical properties.[1,2] In particular, the basal plane conductivity σ_a may be several orders of magnitude larger than the out-of-plane conductivity σ_c.[3] The bonding between intercalate and adjacent graphite planes is at least partially ionic due to a charge transfer between the intercalate species and the graphite host. Stage-1 alkali-metal graphite intercalation compounds,[4] in which the valence electron of the alkali metal is donated to the graphite bonding layers, can thus be described as a sequence of alkali-metal and graphite layers with alternating charges. This out-of-plane ionicity suggests the possibility of a Lyddane-Sachs-Teller (LST)-type splitting[5,6] between the zone-center longitudinal and transverse optic phonons which are polarized parallel to the *c* axis. Such a splitting has been observed in other layered ionic crystals.[7,8] In graphite intercalation compounds this effect should only be present in the parallel polarization. The splitting for the Γ point optical phonons polarized in the graphite basal plane is expected to be quenched by the relatively large in-plane conductivity which should screen the ions effectively. Here, we present an attempt to detect the LST splitting in the donor compound CsC_8 by inelastic neutron scattering.

We intercalated 0.7 cm^3 of pyrolytic graphite (mosaic $=0.8°$) with cesium atoms (stated purity 99.9%) in a two-stage furnace in the usual manner. The stage and homogeneity of the sample were then checked with $(00L)$ elastic neutron scans. The mosaic, after intercalation, was found to be 3°. The phonon groups were obtained using constant-Q scans with the incident neutron energy fixed at 28.0 meV. Graphite was used for both the monochromator and the analyzer. The neutron measurements were performed at room temperature using BT-4, a triple-axis spectrometer located at the National Bureau of Standards Research Reactor.

The previously measured $[00q]$ longitudinal (L) and $[q00]$ transverse (T) phonon dispersion of CsC_8 is shown in Fig. 1.[9] The apparent absence of any splitting between the Γ-point longitudinal phonon $\omega_{L\perp}$ and the transverse phonon $\omega_{T\perp}$, in the region indicated, is not conclusive evidence that such a splitting does not exist, because the spectra were obtained on different instruments under different conditions using relatively poor resolution. Therefore, we have performed a more careful investigation of both branches close to the Γ point. The results of this measurement are shown in Fig. 2, where we have plotted the phonon energies versus q^2 since the dispersion close to the Γ point can be approximated by

$$\omega(q)=\omega_{L,T\perp}+\alpha_{L,T}q^2 \ .$$

Here the $\alpha_{L,T}$ are the slopes of the best-fit lines. This analysis allows one to extract the zone-center energies, $\omega_{L\perp}=(17.42\pm0.06)$ meV and $\omega_{T\perp}=(17.48\pm0.07)$ meV, directly from the $q^2=0$ intercept. From these values one finds the splitting $\Delta\omega_{\text{exp}}=\omega_{L\perp}-\omega_{T\perp}=(-0.06\pm0.09)$ meV. Note that data have been obtained for both $+|q|$ and $-|q|$ and that there is little difference between these two cases for either phonon branch, indicating that the spectrometer was well aligned.

There are two possible explanations for this result: either the splitting exists but is < 0.15 meV, or the splitting is quenched. A simple analysis of the interaction between a transverse optic phonon and the electric field of a photon can be used to estimate the splitting assuming that the ma-

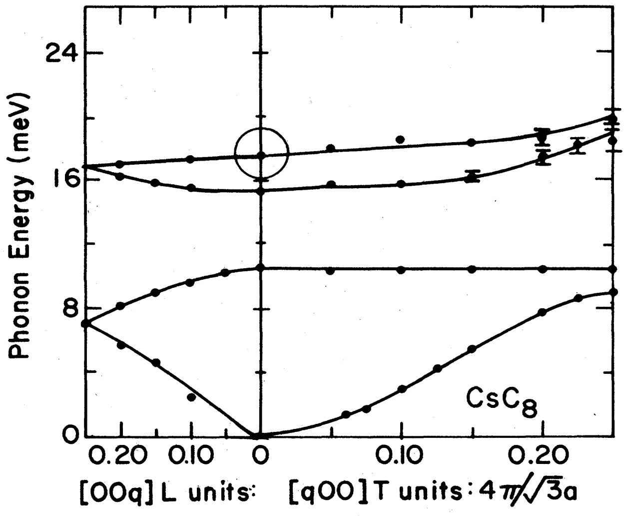

FIG. 1. Phonon dispersion of CsC_8 from Ref. 9. The circle indicates the region which has been carefully probed to reveal any splitting between the zone-center longitudinal and transverse phonons.

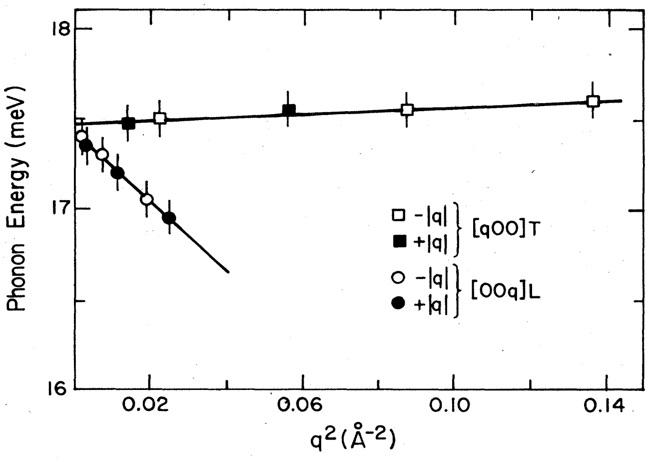

FIG. 2. Energies of the $[q00]$ transverse and $[00q]$ longitudinal phonons plotted as a function of q^2. Using this figure one obtains the zone-center phonon energies $\omega_{L\perp}=(17.42\pm0.06)$ meV and $\omega_{T\perp}=(17.48\pm0.07)$ meV from which the splitting $\Delta\omega_{\text{exp}}=\omega_{L\perp}-\omega_{T\perp}=(-0.06\pm0.09)$ meV is obtained. Phonons have been measured for both $+|q|$ and $-|q|$ to verify proper alignment of the neutron spectrometer.

terial is an ionic insulator. In this model one obtains the approximate relation[10]

$$\Delta\omega_0=\frac{2\pi N f^2 e^2}{\omega_T \mu}\ , \tag{1}$$

where N is the number of ion pairs of reduced mass μ and effective charge fe per unit volume. For CsC_8, this gives $\Delta\omega_0\approx 3$ meV where the charge transfer has been taken to be $f=1$.[11] Thus, it is reasonable to conclude that the LST splitting has been quenched by free-carrier screening.

This quenching can be understood by examining the dielectric constant perpendicular to the graphite planes $\epsilon_\perp(\omega)$. In the absence of free carriers one has[10]

$$\epsilon_\perp(\omega)=\epsilon_\perp(\infty)+\frac{\epsilon_\perp(0)-\epsilon_\perp(\infty)}{1-(\omega/\omega_{T\perp})^2}\ . \tag{2}$$

Here, $\epsilon_\perp(\infty)$ and $\epsilon_\perp(0)$ are the high-frequency and static dielectric constants perpendicular to the planes. The free carriers present in the system can be accounted for by the inclusion of a simple Drude term. Then[12]

$$\epsilon_\perp(\omega)=\epsilon_\perp(\infty)+\frac{\epsilon_\perp(0)-\epsilon_\perp(\infty)}{1-(\omega/\omega_{T\perp})^2}-\frac{\epsilon_\perp(\infty)\omega_{P\perp}^2}{\omega^2}\ , \tag{3}$$

where $\omega_{P\perp}$ is the plasma frequency. The frequencies of both the longitudinal and transverse modes can then be determined using the conditions

$$\epsilon_\perp(\omega)=0 \tag{4}$$

for longitudinal modes and

$$\epsilon_\perp(\omega)=\frac{q^2c^2}{\omega^2} \tag{5}$$

for transverse modes. Note that q^2c^2/ω^2 is extremely large for all values of q measured in this experiment and, therefore, the frequency of the phononlike transverse mode is given by $\omega_{T\perp}$. A graphical determination of the frequencies of the longitudinal modes is shown schematically in Fig. 3 for the cases $\omega_{P\perp}^0 \ll \omega_{T\perp}$ (small free-carrier concentration), $\omega_{P\perp}^0 \lesssim \omega_{T\perp}$, and $\omega_{P\perp}^0 > \omega_{T\perp}$ (large free-carrier concentration) where $\omega_{P\perp}^0$ is the plasma frequency in the absence of any coupling to the longitudinal phonon. Figure 4 then summarizes the frequencies of both longitudinal modes and the transverse phononlike mode as a function of $\omega_{P\perp}^0$. The frequencies of the phononlike excitations appear essentially independent of the uncoupled plasma frequency, while the frequency of the plasmonlike excitation appears as a linear function of $\omega_{P\perp}^0$. Thus, Fig. 4 can be divided into three distinct regions. In region 1 ($\omega_{P\perp}^0 \ll \omega_{T\perp}$) the phononlike modes show the usual LST splitting characteristic of ionic insulators. In region 2 ($\omega_{P\perp}^0 \sim \omega_{T\perp}$) one sees hybridization of the plasmon and the longitudinal phonon. In region 3 ($\omega_{P\perp}^0 \gg \omega_{T\perp}$) the LST splitting has been quenched. From Eq. (3) we find that the residual splitting between the longitudinal and transverse modes in region 3 of Fig. 4 is given by $\Delta\omega_R=-\Delta\omega_0(\omega_{T\perp}/\omega_{P\perp})^2$ where $\Delta\omega_0$ is the splitting in the absence of any free carriers (≈ 3 meV—see above). Since we know $|\Delta\omega_R|<0.15$ meV and $\omega_{T\perp}=17.48$ meV, we may place a lower limit of $\omega_{P\perp}>80$ meV on the plasma

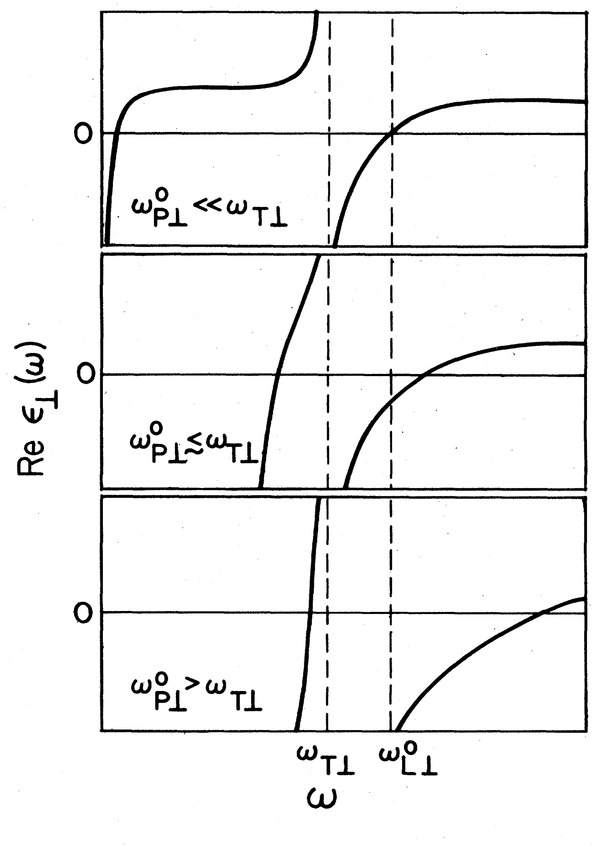

FIG. 3. Frequency dependence of the real part of the dielectric constant perpendicular to the graphite planes for three different values of the uncoupled plasma frequency $\omega_{P\perp}^0$. The transverse phonon frequency $\omega_{T\perp}$ and the uncoupled longitudinal frequency at $\omega_{P\perp}^0=0$ are indicated. The actual frequencies of the coupled longitudinal excitations occur when $\epsilon(\omega)=0$; thus, $\omega_{T\perp}$ effectively serves as a maximum frequency for the lower-frequency longitudinal mode. Using this figure as a guide, one can schematically plot the excitation frequencies as a function of $\omega_{P\perp}^0$ (Fig. 4).

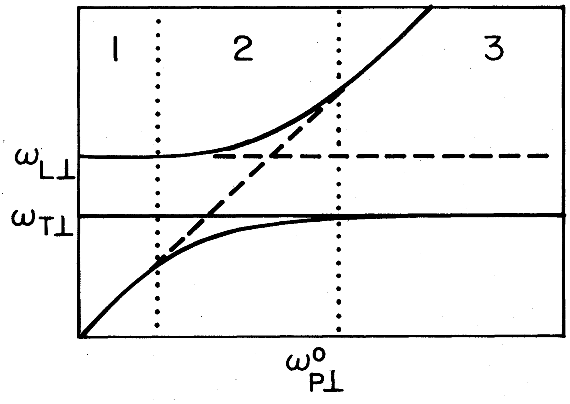

FIG. 4. Frequencies of the three relevant excitations shown schematically as a function of the uncoupled plasma frequency $\omega^0_{P\perp}$. In region 1 ($\omega^0_{P\perp} << \omega_{T\perp}$) one sees two flat phononlike modes which display the LST splitting characteristic of ionic insulators. In region 3 ($\omega^0_{P\perp} >> \omega_{T\perp}$) one again sees two flat phononlike modes; however, the splitting has been effectively quenched. For CsC_8 $\omega_{P\perp} >> \omega_{T\perp}$.

frequency for perpendicular polarization. Reflectance measurements on the compound CsC_8 indicate that $\omega_{P\perp} = 1900$ meV.[13] It is thus reasonable to conclude that the LST splitting is quenched by free-carrier screening.

In order to observe the LST splitting in a layered material, a system with reduced c-axis conductivity ($\omega^2_{P\perp} \propto \sigma_\perp$) and a reasonably large charge transfer ($\Delta\omega \propto f^2$) would be needed. Higher-stage donor compounds have reduced c-axis conductivity and it is known that in the second stage KC_{24} compounds, $\omega_{P\perp} < 200$ meV;[14] therefore, it is possible that the LST splitting may occur in this compound. Acceptor compounds exhibit extremely large anisotropies, but are known to have small charge transfers, thus making the LST splitting difficult to observe. Recent neutron scattering measurements of the phonon dispersion in the acceptor compound C_7Br show no apparent LST splitting.[15]

In conclusion, we have found no apparent LST splitting for phonons polarized parallel to the c axis in the graphite intercalation compound CsC_8 and have attributed this result to the relatively large value of the c-axis plasma frequency which effectively screens ionic motion along the c axis.

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