Neutron scattering study of phonon-libron coupling in potassium-ammonia intercalated graphite

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We present the results of an inelastic neutron scattering study of the $[001]L$ lattice dynamics of stage-1 and stage-2 K-ammonia intercalated graphite. The results show that a librational mode splits the acoustic-phonon branch of the stage-1 compound at an energy of about 7 meV and that the interaction between the ammonia molecules in different galleries is very weak. This effect can be described by a simple one-force-constant Born–von Kármán model with the libration treated as an Einstein oscillator and the hybridization follows from a phonon-libron coupling term. The nature of this additional mode, however, remains to be determined. In addition, we report that the elastic constant C_{33} is considerably softer in the K-ammonia system than in the analogous binary K compounds.

INTRODUCTION

Molecular crystals are a class of solids in which some of the constituent atoms are tightly bound in a molecular unit which in turn is more loosely bound to the surrounding atoms or molecules. Because of the wide variety of dynamical phenomena and orientational phase transitions that they display, crystals of this type have been extensively studied.[1-4] Neutron scattering is perhaps the most powerful tool to elucidate the excitational properties such as phonon dispersion, intramolecular modes, molecular rotations and rotational tunneling, translational diffusion, and librational modes ("vibrational" excitations where the molecule oscillates as a single unit) in these rich dynamical systems.

Of the many molecular solids which have been studied using inelastic or quasielectric neutron scattering techniques, several have been layered or have had some other two-dimensional aspect to their structure.[5] These systems include water intercalated in various forms of montmorillonite, vermiculite, and hectorite;[6-8] methane, ethane, ethylene, butane, and ammonia adsorbed on the surface of graphite;[9-14] ammonia intercalated in TaS$_2$;[15] and H$_2$ and HNO$_3$ intercalated in graphite;[16-19] In each of these cases the molecular species contains hydrogen which has a very large, incoherent thermal-neutron scattering cross section. Thus an inelastic scattering experiment will determine the vibrational density of states and any internal modes, librational states, or translational lattice modes will be manifested as peaks in the spectrum. However, much more detailed information about the interactions can be obtained via coherent neutron scattering due to the ability to measure the wave-vector dependence of the excitations. One common example of this advantage is the measurement of phonon dispersion relations using coherent scattering as opposed to the measurement of the phonon density of states using incoherent scattering. This has been exploited in only a limited number of studies of layered molecular crystals.[20,21] Another advantage is the ability to measure the details of the interactions between elementary excitations in a solid. The most studied isotropic systems in this regard are the mixed alkali halide cyanides. In the low-cyanide-concentration limit, neutron scattering results show that the [110] transverse-acoustic branch (polarization $[1\bar{1}0]$) is split due to phonon-libron hybridization.[22,23] Here we present the first coherent, inelastic neutron scattering study of phonon-libron coupling in a layered system, K-ammonia intercalated graphite.

Despite the fact that K-ammonia intercalated graphite was first synthesized over 30 years ago,[24] studies of the structure of KC$_{24}$(NH$_3$)$_x$ with $0 < x < 4.3$ have appeared only very recently.[25-27] These have shown that in the "saturated" compound, KC$_{24}$(NH$_3$)$_{4.3}$, the intercalate layer is a two-dimensional liquid at room temperature and that the liquid structure factor can be reasonably well accounted for by a model in which four ammonia molecules are loosely associated with a single K ion and the rest of the ND$_3$ molecules are "free" (Fig. 1). In addition, NMR spectra have indicated that on the average, the molecular threefold-symmetry axis lies in the basal plane of the graphite.[28-30] Thus the K-ammonia layers form the two-dimensional structural analogue of three-dimensional metal-ammonia solutions.[31,32] Furthermore, observed resistivity anomalies as a function of ammonia concentration have recently been interpreted in terms of a two-dimensional metal-insulator transition.[33,34] This analysis depends crucially on the back transfer of elec-
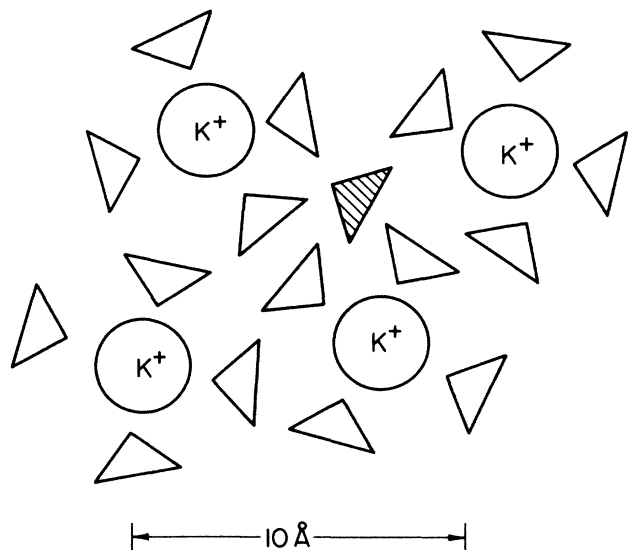
FIG. 1. Schematic diagram of the in-plane structure of $KC_{24}(ND_3)_{4.3}$. The circles represent K ions, the open triangles represent ND_3 molecules which are associated with a K ion, and the shaded triangle represents a "free" ammonia molecule.

trons[28,35] from the carbon plane to the intercalate layer where they are then solvated or "caged."[36] This back-transfer effect, along with the lattice expansion from 5.35 Å for KC_8 to 6.63 Å for $KC_{24}(ND_3)_{4.3}$, implies that the intercalate-graphite force constant ϕ, manifested in the [001] longitudinal phonon dispersion, may be reduced in the K-ammonia compound compared to the binary stage-1 compound KC_8 and that ϕ must vary with the ND_3 concentration. We have therefore measured these phonons for three different compounds, stage-1 $KC_{24}(ND_3)_{4.3}$, stage-1 $KC_{22}(ND_3)_{3.1}$, and stage-2 $KC_{28}(ND_3)_{2.3}$.

EXPERIMENTAL PROCEDURE

The samples used in this study were prepared by cutting pyrolytic graphite, with a typical mosaic spread of 5°, into 30 pieces of dimension $1.5 \times 1.0 \times 0.1$ cm^3. These pieces were then intercalated, using the standard two-bulb method to form the binary stage-2 compound KC_{24}, after which they were removed from the glass in a glove box, and arranged in an aluminum spacer assembly with their c axis well aligned. The assembly was then placed in an aluminum sample can which was compression sealed with a tapered stainless-steel cap.[37] A stainless-steel bellows valve was welded to the cap to allow the evacuation of the sample holder and the admission of the ammonia vapor. The deuterated ammonia, used to enhance the coherent scattering, had an initial purity of 99.95% and was purified further by repeated exposure to sodium metal.[32,35] The actual ammoniation of the sample was performed *in situ* using a vapor pressure of about 9.5 atm maintained by keeping the remote liquid-ammonia reservoir at room temperature. The co-

intercalation was monitored with repeated (00*l*) scans. Three hours of exposure to ammonia were required before the (00*l*) scan, indicative of a pure stage-1 sample and shown in Fig. 2, was achieved. At this point, the ammonia fraction, determined by measuring the ammonia pressure and then using the previously measured pressure dependence of x,[35] was $x = 4.3$. The observed lattice-parameter shift upon co-intercalation was also consistent with that measured by York and Solin.[35] After all measurements were performed at $x = 4.3$, the ND_3 concentration was then reduced to $x = 3.1$ by slowly removing ammonia vapor until a pressure of 0.20 atm was present in the sample can. Again the ammonia fraction was determined using the results of York and Solin.[35] The stage-2 sample was similarly prepared. However, the co-intercalation process was halted when the stage-2 compound $KC_{28}(ND_3)_{2.3}$ was formed. Neither the stage-2 compound nor the $x = 3.1$ compounds were pure-phase samples (as was also found in Ref. 35). However, in both cases the phase of interest was the dominant phase, and all phonons were measured in more than one Brillouin zone to assure that they were indeed associated with the periodicity of this phase.

The neutron scattering results presented here were obtained using two triple-axis spectrometers (BT4, stage 1; BT9, stage 2) located at the National Bureau of Standards Reactor. Both spectrometers were equipped with graphite monochromator and analyzer crystals [(002) reflection]. All of the data presented here were acquired in the constant-Q mode and most were obtained with a fixed final energy of 13.7 meV and a collimation of 40'-20'-40'-40' for the acoustic branch and 40'-40'-40'-80' for the optic modes. Other instrumental configurations were also used to eliminate the possibility that any of the features observed in the scattering were spurious. All of the measurements presented here were performed at room temperature.
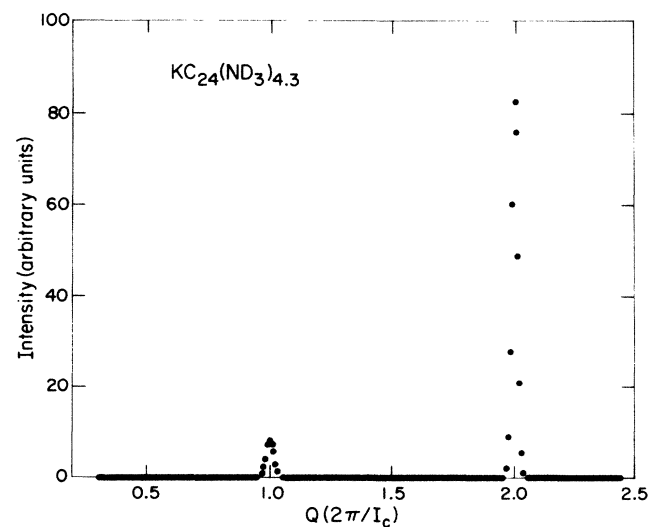

FIG. 2. An (00*l*) elastic scan of the $KC_{24}(ND_3)_{4.3}$ sample showing that it is a pure stage-1 compound. The c-axis lattice parameter I_c was found to be 6.635 Å for this composition.

RESULTS

The measured energies of the [001] longitudinal-phonon modes of stage-1 $KC_{24}(ND_3)_{4.3}$ are shown in Fig. 3(a). Three branches are clearly observed; however, it is well known that stage-1 compounds typically display only two [001]L modes because the c-axis repeat distance comprises two planes with different areal mass densities.[38] Comparison with these simple stage-1 compounds
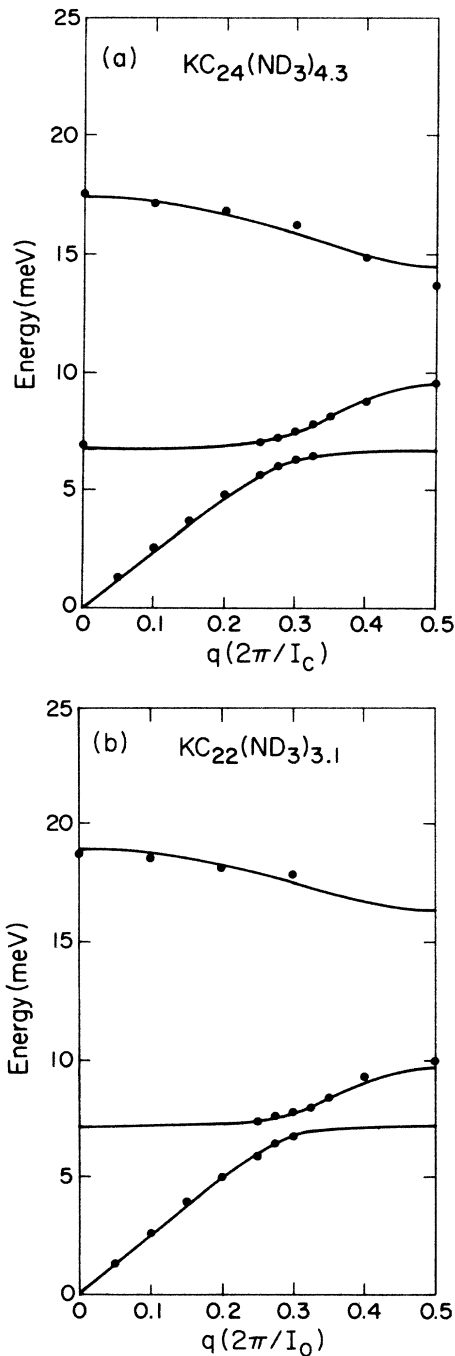

FIG. 3. (a) [001]L phonon dispersion of the stage-1 compound $KC_{24}(ND_3)_{4.3}$. The solid line represents the model discussed in the text. (b) [001]L phonon dispersion of the stage-1 compound $KC_{22}(ND_3)_{3.1}$.

indicates that the lower two branches of $KC_{24}(ND_3)_{4.3}$ belong to the same acoustic branch which has been split by the hybridization of the phonons with an additional excitation at about 7 meV. As will be discussed later, however, the nature of this mode is not yet certain but it must be associated with librations of the ammonia molecules. The [001]L modes of the stage-1 compound $KC_{22}(ND_3)_{3.1}$ are shown in Fig. 3(b). Note that the phonon-libron coupling is also present in this compound, although the librational energy has increased slightly and the splitting of the acoustic branch has been reduced compared to the compound with the higher ammonia concentration.

The crossover from phononlike to libronlike excitations in $KC_{24}(ND_3)_{4.3}$ is clearly shown in Fig. 4 where the groups are displayed at three different values of the wave vector q. The solid line represents a two-Gaussian
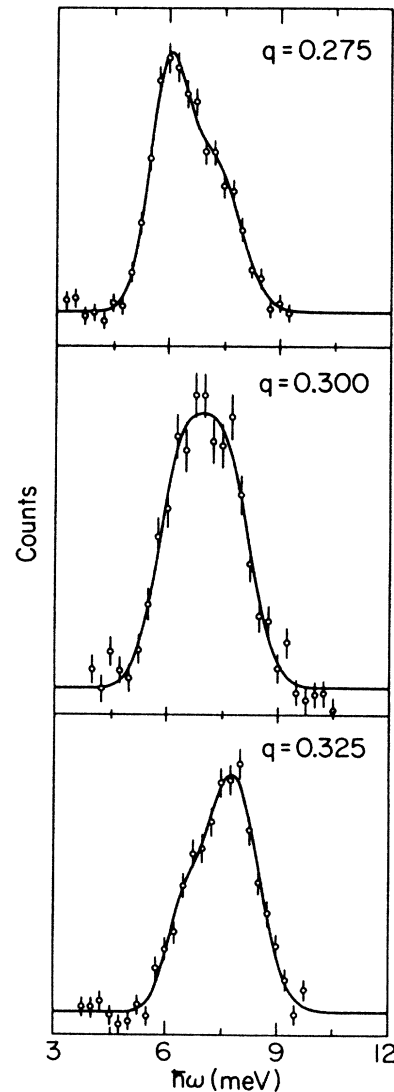

FIG. 4. Coupled phonon-libron groups at $q = 0.275$, 0.300, and 0.325 [$Q = (0,0,3.275)$, $(0,0,3.300)$, and $(0,0,3.325)$] for the compound $KC_{24}(ND_3)_{4.3}$. The solid lines represent fits to the sum of two Gaussian-shaped peaks. The positions from these fits were plotted as points in Fig. 3.

fit to the experimental data. (The peak positions of these fits are plotted as circles in Fig. 2.) For both $q = 0.275$ and 0.325 [$Q = (0,0,3.275)$ and $(0,0,3.325)$], the width of the more intense peak is nearly resolution limited while the less intense peak is broadened compared to the resolution function. At $q = 0.300$ [$Q = (0,0,3.300)$], the two peaks have nearly equal intensities and widths again broadened compared to the instrumental resolution. Thus, one sees that as a particular branch assumes librational behavior it broadens and loses intensity. In an attempt to observe the librational mode directly, we have performed the scan shown in Fig. 5. The value of the scattering vector $Q = (0,0,3)$ ($q = 0$) was chosen in order to avoid inelastic scattering from nearby phonons which would easily have obscured the observed feature. The solid line again represents a two-Gaussian fit to the data. The first Gaussian was chosen to represent the "background" from other inelastic processes as well as the elastic scattering. The other Gaussian, representing the librational mode, was then found to have an energy of 7.1 meV and a width much broader than the instrumental resolution of 1.1 meV. Note that the libron excitation energy is in good agreement with the value observed in the phonon-libron coupling region. This indicates that the librational excitation is essentially dispersionless along the c axis, implying that there is no specific phase relation between the librational oscillations in adjacent galleries.
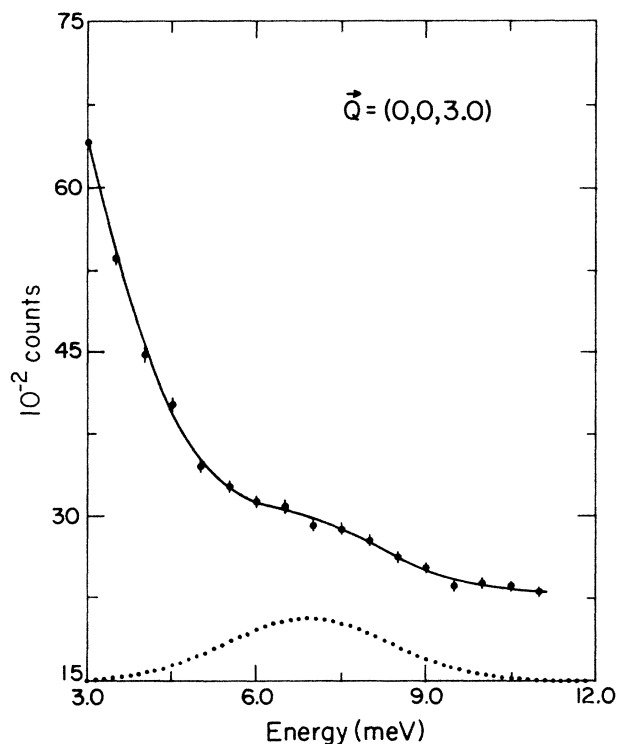
Therefore the interlayer interaction between ammonia molecules must be weak, in agreement with the complete absence of positional correlations observed in the elastic scattering data.[27]

The measured phonon dispersion of the stage-2 compound $KC_{28}(ND_3)_{2.3}$ is shown in Fig. 6. Despite considerable effort, no scattering which could be unambiguously identified as the upper optical mode could be found. It should also be noted that the energy of the librational mode in the stage-1 compound falls within the Brillouin-zone boundary gap of the stage-2 compound and thus a coupled phonon-libron mode would not be observable if in fact the librational excitation exists near 7 meV in $KC_{28}(ND_3)_{2.3}$.[39] Therefore, in order to determine whether or not the libration does occur in this stage-2 compound, one would have to observe the excitation directly and unambiguously. This was not possible because the stage-2 sample was not a pure phase, so that some stage-1 regions were also present. Thus since there is no Q dependence of the librational energy, one could not ascertain whether any observed scattering was due to a libration in the stage-2 compound or if it came from the stage-1 regions known to display such a mode. Furthermore, at these temperatures, the lifetime of the excitation is quite small (Fig. 5) which compounds the difficulty.

DISCUSSION

We have modeled the observed dispersion relation using a 3×3 dynamical matrix, D, which includes a virtual-crystal, one-force-constant Born–von Kármán model, an Einstein oscillator of energy α representing the libration, and a term containing the coupling constant γ:
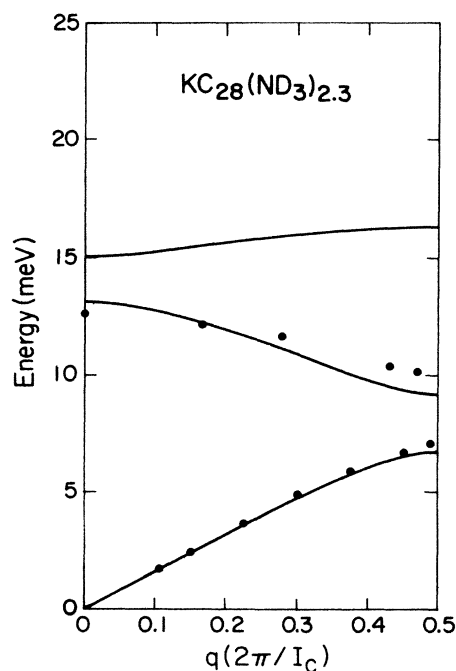

FIG. 5. Inelastic scan at $q = 0.00$ [$Q = (0,0,3)$] for the stage-1 compound $KC_{24}(ND_3)_{4.3}$. The solid line is a fit to two Gaussian functions, the first of which was chosen to represent the background. The second peak, indicated by the dots, then represents the librational excitation and was found to have an energy of 7.1 meV.

FIG. 6. [001]L phonon dispersion of stage-2 $KC_{28}(ND_3)_{2.3}$. The solid line represents the simple, two-force-constant Born–von Kármán model discussed in the text.

$$D = \begin{bmatrix} \dfrac{2\phi}{M} & \dfrac{-\phi}{\sqrt{mM}}(1+e^{iql_c}) & -\gamma\alpha(1-e^{i2ql_c}) \\[2mm] \dfrac{-\phi}{\sqrt{mM}}(1+e^{-iql_c}) & \dfrac{2\phi}{m} & 0 \\[2mm] -\gamma\alpha(1-e^{-i2ql_c}) & 0 & \alpha^2 \end{bmatrix} . \tag{1}$$

Here ϕ is the intercalate-graphite force constant per carbon atom, M is the areal carbon mass density, m is the areal intercalate mass density per carbon atom, and I_c is the c-axis lattice constant. The 2×2 matrix forming the upper left corner represents the uncoupled phonon dispersion. The positive square roots of the eigenvalues of this matrix are shown as the solid lines in Fig. 3. The best-fit parameters corresponding to these dispersion relations are given in Table I. The slight reduction of the librational energy with increasing ammonia concentration is consistent with the fact that the c-axis lattice parameter increases as the ammonia concentration increases, reducing the curvature of the potential and therefore, the energy of the libration. In addition, note that the coupling parameter γ scales approximately with the ammonia concentration (Fig. 7). Thus the librations couple individually to the phonons, another indication that the librations are localized within individual intercalate layers. It should also be pointed out that ϕ, the force constant per carbon atom, is essentially independent of the ND_3 concentration. This seems to imply that the K-graphite interaction makes the dominant contribution to ϕ since the K-to-C ratio is much more nearly constant than the ND_3 concentration for the compounds in question, and suggests that the elastic interaction is more important than the electrostatic interaction in determining the value of the intercalate-graphite force constant.[20,35] In addition, it should be noted that the small change in the K-to-C ratio, the small change in the c-axis lattice constant, and a charge back-transfer effect all tend to decrease ϕ as the ND_3 composition, x, is increased, while the total ammonia-graphite interaction must strengthen at least somewhat as x increases. Thus it is extremely difficult to draw any conclusions concerning possible charge transfer effects from the present data. In contrast, the binary alkali-metal–graphite intercalation compounds display nearest-neighbor force constants which

are nearly the same per intercalate atom, not per C atom. This implies that the intercalate-graphite interaction in those compounds arises from a single physical process, presumably dominated by the donation of the outer s electron from the alkali-metal atom to the carbon sheet.

Since it was impossible to find the second optic mode in the stage-2 compound, we were unable to fit the data in an unambiguous way. The solid line in Fig. 6 is simply a two-parameter Born–von Kármán model which uses the intercalate-graphite force constant, $\phi=2100$ dyn/cm, obtained from the stage-1 results and determined to be independent of the intercalate concentration. In addition, a graphite-graphite nearest-neighbor force constant of 2900 dyn/cm, consistent with the values obtained for the stage-2 binary compounds,[38] was assumed. While the agreement is certainly not perfect, there is a reasonable correspondence between the data and the model.

In Table II, the sound velocity v_s and elastic constant C_{33}, determined from the initial slope of the acoustic branch, are given for $KC_{24}(ND_3)_x$ and compared to the values for the stage-1 KC_8.[38,40] There is basically no difference between the two compositions of the K-ammonia compound studied here, but both y_s and C_{33} are substantially reduced compared to the binary KC_8. Earlier, two possible reasons for this reduction were proposed. The first, and certainly the most important, effect was simply the large expansion of the interlayer spacing of the ternary compound. The other possible reason mentioned in the Introduction was the back transfer of charge to the intercalate layer in the K-ammonia compound. However, the previous discussion concerning ϕ implies that this electronic effect is unimportant within the accuracy of the present study. The values for the

TABLE I. Best-fit parameters for the $[001]L$ modes of two stage-1 K-ammonia intercalated-graphite compounds. Here ϕ represents the intercalate-graphite nearest-neighbor force constant, α is the energy of the Einstein oscillator, and γ is the coupling constant. The nearest-neighbor force constant for the stage-1 compound KC_8 is included for comparison. The force constants are normalized per carbon atom.

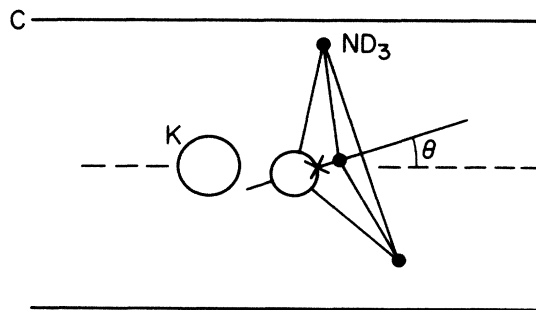| Compound	ϕ (dyn/cm)	α (meV)	γ (meV)
$KC_{24}(ND_3)_{4.3}$	2090	6.7	0.70
$KC_{22}(ND_3)_{3.1}$	2120	7.1	0.49
KC_8	4140[a]		

[a]Reference 38.

FIG. 7. Schematic diagram showing a librational mode of the ammonia molecule about its center of mass represented by the $\times$. Here θ is the rotational coordinate discussed in the text. A simple estimate of the energy of such an excitation yields a value of 25 meV, while the observed value is 7 meV.

TABLE II. Elastic constants and sound velocities for K-ammonia intercalated graphite along with the same quantities for the analogous binary compounds.

Compound	Stage	C_{33} (10^{11} dyn/cm)	v_s (10^5 cm/s)
$KC_{24}(ND_3)_{4.3}$	1	1.71±0.10	3.22±0.10
$KC_{22}(ND_3)_{3.1}$	1	1.62±0.10	3.18±0.10
$KC_{28}(ND_3)_{2.3}$	2	2.94±0.09	3.90±0.06
KC_8	1	4.85±0.14[a]	4.91±0.07[a]
KC_{24}	2	3.71±0.15[a]	4.33±0.15[a]

[a]Reference 38.

sound velocity and C_{33} for the stage-2 ternary compound are also given in Table II along with the results for the binary stage-2 compound KC_{24}. While the softening of the ternary compared to the binary compound is apparent for the stage-2 compounds, it is not nearly as dramatic as it was for stage-1. One reason is simply that the stage-2 binary is softer than the stage-1 binary due to the different in-plane intercalate densities in these materials.[38] Another is that the stage-2 ternary compound contains fewer soft intercalate-graphite bonds than the stage-1 ternary, thereby increasing C_{33} in the stage-2 K-ammonia compound relative to its stage-1 counterpart.

The width of the librational peak indicates that the librational potential is quite anharmonic. In light of quasi-elastic neutron scattering results which reveal the intercalate layer to be a rather mobile, two-dimensional molecular liquid at room temperature,[41] it is actually much more difficult to understand why the librational excitation is not broadened to the point where it is completely unobservable. In fact at Q's of 3 Å^{-1}, the results of Ref. 41 indicate that the low-frequency in-plane motion of the liquid can be characterized as a complicated combination of translational diffusion and reorientations of the fourfold molecular complexes which occur on a time scale only somewhat longer than the period of the libration. Naturally, this effect would also lead to a broadening of the observed libron spectrum. To partially reconcile this difficulty we note that this material is a one-dimensional solid along the c axis, the direction in which the scattering vector was oriented. It has also been observed that the quasielastic scattering in the liquid intercalate phase is narrower and less intense when Q is directed parallel to $\hat{c}$. This implies that the potential is somewhat stronger and better defined for oscillations occurring mostly out of the basal plane (the "solidlike" direction) compared to those occurring in the basal plane (the "liquidlike" direction).

The actual physical motion which corresponds to the observed librational excitation has not been unambiguously determined; however, it is possible to make a reasonable speculation. From the quasielastic neutron scattering results presented elsewhere[41] and from NMR results,[30] it is clear that there is a rotation which persists to low temperatures. A physically reasonable assignment for this motion is a rotation about the threefold molecular axis C_3. The fact that this component of the quasielastic line broadens to an essentially flat background at

room temperature, implying almost-free rotation, indicates that the libration is not about the ammonia C_3 symmetry axis. This leaves two possible assignments for the motion, assuming that it can be characterized as a libration of individual molecules, both of which involve oscillations of the molecular dipole moment (i.e., the C_3 symmetry axis) with respect to the K ion. A simple model for such excitations is obtained by noting that this is also the axis along which the molecular dipole moment is directed and that the K atoms are almost completely ionized. The potential energy U of such a system is given by

$$U = - \left[\frac{pe}{R^2} \right] \cos\theta , \qquad (2)$$

where θ describes the angle that the dipole moment $\mathbf{p}$ makes with the line connecting the position of the point charge and the position of the dipole, and R is the separation between the ion and the molecule. Note that when $\theta = 0$ the dipole points directly away from the charge, that is the N atom is nearest to the K^+ ion. The librational frequency is then given by

$$\omega_{\text{lib}} = \left[\frac{pe}{R^2 I} \right]^{1/2} , \qquad (3)$$

where I is the moment of inertia about the librational axis. For ND_3, $p = 1.3$ D, $I_{\text{c.m.}} \simeq 3 \times 10^{12}$ meV Å^2/c^2 (c is the speed of light), and the metal-ammonia distance is roughly 3 Å. This gives an energy for librations occurring about the molecular center-of-mass of about 25 meV, far different from the observed value of 7 meV (Fig. 7). It is however, interesting to note that this estimate is in good agreement with the value of 23 meV obtained using the phenomenological potential $U = U_0 \cos(2\theta)$ with $U_0 = 100$ meV which was postulated by Tsang et al. in Ref. 29. In either case the barrier is an order of magnitude too large to explain the energy of the observed excitation. However, if the barrier was a factor of 10 smaller, it would then be comparable to the thermal energy (25 meV) and one would expect to observe thermally activated reorientations of the C_3 axis. In addition, the low barrier required to account for such a single molecule mode implies that anharmonicity would render the librational excitation, as well as the coupling to the acoustic phonons, unobservable, which is clearly not the case.

The only way to resolve these difficulties is to find a mechanism which increases the effective moment of inertia thereby leaving the potential barrier high enough to account for the relatively small degree of anharmonicity which was observed. This can be done in two ways. The first is to shift the rotational axis away from the molecular center-of-mass thereby increasing the moment of inertia via the parallel-axis theorem. It can easily be shown that this displacement must be 1.3 Å in order to reduce the librational energy from 23 meV to the observed value of 7 meV. Note that this places the rotational axis outside the pyramid formed by the nuclei of the N and D atoms and that 1.3 Å is essentially half of the K-ammonia distance determined from the elastic scattering results.[27] It is thus tempting to ascribe the observed excitation to a K-ammonia "bond-bending" mode (Fig. 8). The facts
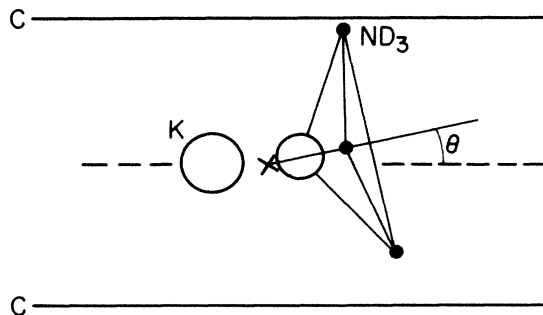
FIG. 8. Schematic diagram showing a librational mode of the ammonia molecule about the center of the K-ammonia "bond" represented by the ×. Here θ is the rotational coordinate discussed in the text. This model yields a librational energy of about 7 meV in agreement with the observed value.

that the excitation couples to phonons which are polarized out of the graphite basal plane; that reorientations of the metal-ammonia complexes have been observed by quasielectric neutron scattering;[41] and that NMR results indicate that the out-of-plane potential is approximately what is required to account for a 7-meV bond-bending mode,[29] all suggest that the motion occurs principally out of the basal plane. It is also encouraging to note that the librational energy is not extremely sensitive to the distance between the rotational axis and the molecular center-of-mass. Thus the liquid nature of the intercalate would not be expected to significantly broaden a bond-bending excitation occurring in the solidlike direction.

The other mechanism by which the effective moment of inertia could increase is if the observed mode is due to a collective excitation and not due to the motion of individual molecules as has been previously assumed. Since the quasielectric scattering data[41] indicates that the four-fold ammonia-K complexes reorient in the basal plane, it is natural to suggest that the libron involves the ammonia molecules within a single one of these complexes. The fact that such an excitation would take place mostly in the basal plane does not completely eliminate it from consideration since the observed splitting of the $[001]L$ acoustic branch in the stage-2 binary alkali-metal–graphite intercalation compounds was found to be attributable to a coupling between in-plane motions of

the intercalate atoms and these same out-of-plane phonons.[42,43] Thus while the bond-bending model seems to explain the observations in a relatively complete fashion, it is not the only model which seems to be capable of so doing. Further experiments are therefore necessary to unambiguously determine which, if either, of these models are appropriate for K-ammonia intercalated graphite.

CONCLUSION

We have measured the $[001]L$ phonon dispersion in three K-ammonia intercalated graphite compounds and have observed that the lattice is appreciably softer than is the case for the binary alkali-metal–graphite compounds. We have also observed a librational mode of the ammonia molecules which splits the acoustic branch at an energy of ~ 7 meV. While the present results seem to favor the identification of the observed libron as a K-ammonia bond-bending mode, further experiments are necessary in order to unambiguously determine the nature of this excitation. It is clear, however, that it does not correspond to a single particle oscillation about the molecular center-of-mass.

Our results also show that the graphite-intercalate force constant ϕ does not depend on the ammonia concentration, indicating that ϕ is mostly determined by elastic, rather than electrostatic, forces. Recent NMR results[28] indicate that for an ammonia concentration of 4.0, the charge back transfer from the graphite to the intercalate layers is about 0.16 e^-/K-atom. This may be too small to cause an observable change in ϕ. Therefore our results do not contradict claims that the back transfer of charge is responsible for the observed anomalies in the in-plane resistivity.[34] Rather the inelastic scattering data do not appear to be highly sensitive to this affect.

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[1]J. A. Janik, Phys. Rep. **66**, 1 (1980).

[2]J. J. Rush and J. M. Rowe, Physica B + C **137B**, 169 (1986).

[3]W. Press, *Single Particle Rotations in Molecular Crystals*, Vol. 92 of *Springer Tracts in Modern Physics* (Springer-Verlag, Berlin, 1981).

[4]J. W. White, in *Dynamics of Solids and Liquids by Neutron Scattering*, Vol. 3 of *Springer Topics in Current Physics*, edited by S. W. Lovesey and T. Springer (Springer-Verlag, Berlin, 1977), p. 197.

[5]R. K. Thomas, Prog. Solid State Chem. **14**, 1 (1982).

[6]S. Olejnik and J. W. White, Nature (London) **236**, 15 (1972).

[7]J. Conard, H. Estrade-Szwarckopf, A. J. Dianoux, and C. Poinsignon, J. Phys. (Paris) **45**, 1361 (1984).

[8]J. M. Adams, C. Breen, and C. Riekel, Clays Clay Miner. **27**, 140 (1979).

[9]P. Thorel, J. P. Coulomb, and M. Bienfait, Surf. Sci. **114**, L43 (1982).

[10]F. Y. Hansen, R. Wang, H. Taub, H. Shechter, D. G. Reichel, H. R. Danner, and G. P. Alldredge, Phys. Rev. Lett. **53**, 572 (1984).

[11]M. W. Newberry, T. Rayment, M. V. Smalley, R. K. Thomas, and J. W. White, Chem. Phys. Lett. **59**, 461 (1978).

[12]B. H. Grier, L. Passell, J. Eckert, H. Patterson, D. Richter, and R. J. Rollefson, Phys. Rev. Lett. **53**, 814 (1984).

[13]R. Wang, H. Taub, H. J. Lauter, J. P. Biberian, and J. Suzanne, J. Chem. Phys. **82**, 3465 (1985).

[14]P. H. Gamlen, R. K. Thomas, T. D. Trewern, G. Bomchil, N. M. Harris, M. Leslie, J. Tabony, and J. W. White, J. Chem. Soc. Faraday Trans. 1 **75**, 1553 (1979).

[15]C. Riekel, A. Heidemann, B. E. F. Fender, and G. C. Stirling, J. Chem. Phys. **71**, 530 (1979).

[16]J. P. Beaufils, T. L. Crowley, T. Rayment, R. K. Thomas, and J. W. White, Mol. Phys. **44**, 1257 (1981).

[17]I. P. Jackson and J. W. White, Chem. Phys. Lett. **134**, 397 (1987).

[18]F. Batallan, I. Rosenman, A. Magerl, and H. Fuzellier, Phys. Rev. B **32**, 4810 (1985).

[19]I. Rosenman, Ch. Simon, F. Batallan, and A. Magerl, Europhys. Lett. **3**, 1013 (1987).

[20]P. C. Eklund, E. T. Arakawa, J. L. Zarestky, W. A. Kamitakahara, and G. D. Mahan, Synth. Met. **12**, 97 (1985).

[21]D. J. Cebula, M. C. Owen, C. Skinner, W. G. Stirling, and R. K. Thomas, Clay Miner. **17**, 195 (1982).

[22]D. Walton, H. A. Mook, and R. M. Nicklow, Phys. Rev. Lett. **33**, 412 (1974).

[23]J. M. Rowe, J. J. Rush, S. M. Shapiro, D. G. Hinks, and S. Susman, Phys. Rev. B **21**, 4863 (1980).

[24]W. Rudorff and E. Schultze, Angew. Chem. **66**, 305 (1954).

[25]X. W. Qian, D. R. Stump, B. R. York, and S. A. Solin, Phys. Rev. Lett. **54**, 1271 (1985).

[26]X. W. Qian, D. R. Stump, and S. A. Solin, Phys. Rev. B **33**, 5756 (1986).

[27]Y. B. Fan, S. A. Solin, D. A. Neumann, H. Zabel, and J. J. Rush, Phys. Rev. B **36**, 3386 (1987).

[28]T. Tsang, R. M. Fronko, H. A. Resing, X. W. Qian, and S. A. Solin, Solid State Commun. **62**, 117 (1987).

[29]T. Tsang, R. M. Fronko, H. A. Resing, X. W. Qian, and S. A. Solin, Solid State Commun. **63**, 361 (1987).

[30]R. M. Fronko, T. Tsang, H. A. Resing, X. W. Qian, and S. A. Solin (unpublished).

[31]J. L. Dye, Prog. Inorg. Chem. **32**, 327 (1984).

[32]J. C. Thompson, *Electrons in Liquid Ammonia* (Clarendon, Oxford, 1976).

[33]Y. Y. Huang, Y. B. Fan, S. A. Solin, J. Heremans, G. G. Tibbetts, J. M. Zhang, and P. C. Eklund, in *Graphite Intercalation Compounds,* edited by M. S. Dresselhaus, G. Dresselhaus, and S. A. Solin (Materials Research Society, Pittsburgh, 1986), p. 146.

[34]Y. Y. Huang, Y. B. Fan, S. A. Solin, J. M. Zhang, P. C. Eklund, J. Heremans, and G. G. Tibbetts, Solid State Commun. **64**, 443 (1987).

[35]B. R. York and S. A. Solin, Phys. Rev. B **25**, 2463 (1982).

[36]D. M. Hoffman, A. M. Rao, G. L. Doll, P. C. Eklund, B. R. York, and S. A. Solin, in *Graphite Intercalation Compounds,* edited by P. C. Eklund, M. S. Dresselhaus, and G. Dresselhaus (Materials Research Society, Pittsburgh, 1984), p. 237.

[37]H. Zabel, Rev. Sci. Instrum. **54**, 1413 (1983).

[38]H. Zabel and A. Magerl, Phys. Rev. B **25**, 2463 (1982).

[39]One would actually expect the librational energy to be slightly increased in the stage-2 compound (a few tenths of a meV) due to the reduced gallery spacing resulting from the lower ammonia concentration within the intercalate layer.

[40]D. A. Neumann, H. Zabel, J. J. Rush, and N. Berk, Phys. Rev. Lett. **53**, 56 (1984).

[41]D. A. Neumann, H. Zabel, J. J. Rush, Y. B. Fan, and S. A. Solin, J. Phys. C **20**, L761 (1987).

[42]A. Funahashi, T. Kondow, and M. Iizumi, Solid State Commun. **44**, 1515 (1982).

[43]A. Magerl, H. Zabel, and J. J. Rush, Synth. Met. **7**, 339 (1983).