Local modes in $Rb_{1-c}K_c$ alloys: A neutron scattering study

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The lattice dynamics of $Rb_{1-c}K_c$ alloys with $c = 0.06$, 0.18, and 0.29 have been investigated by neutron scattering, using crystals grown for the experiment by a modified Bridgman method. Local modes associated with the K atoms are observed which, as c is increased, rise in frequency, increase in intensity and begin to exhibit noticeable dispersion. The local-mode intensity exhibits a strong wave-vector dependence whose form does not change much with c. At the zone-boundary point N, $(2\pi/a)(2.5, 2.5, 0)$ in $Rb_{0.71}K_{0.29}$, the local mode is about three times as intense as the band mode. It is apparent that, as $c \to 1$, the local mode must evolve into the band mode of pure K. A substantial broadening of the local mode is also apparent at this wave vector and concentration, probably indicating the presence of local environment effects. We compare our results with coherent-potential-approximation calculations, both with and without inclusion of force-constant disorder. The calculations, carried out by Mostoller and Kaplan, and independently by Grünewald and Scharnberg, indicate a softening in the nearest-neighbor Rb-K force constants of about 15% relative to the Rb-Rb force constants. We also compare our results with molecular-dynamics calculations by Jacucci, Klein, and Taylor.

I. INTRODUCTION

The phonon spectra of random substitutional alloys can differ considerably in character from those of pure materials. Localized vibrational states may be formed, and all phonons acquire broadening and shifts in energy arising from the disorder. Coherent inelastic neutron scattering can provide detailed information about the alloy dynamics, since the frequencies and widths of phonons with preselected polarizations and wave vectors can be measured. In this paper the results of an experiment on single crystals of $Rb_{1-c}K_c$ alloys are reported.[1] The potassium atoms in these alloys, because of their smaller mass $(M_{Rb}/M_K = 2.18)$, tend to vibrate in modes with vibrational amplitudes spatially localized around the K sites, and with frequencies above those of the Rb host lattice. The purpose of this experiment is to observe the character of the phonon spectrum as c is increased from a relatively dilute case $(c = 0.06)$ to a high-concentration case $(c = 0.29)$. This c range is of special interest, since it is here that the local modes will begin to acquire an observable energy broadening and to change in character to propagating excitations. The ability to predict phonon line shapes in the neutron scattering law $S(\vec{Q}, \omega)$ provides a stringent test for theories of the lattice dynamics of alloys.

The theory of excitations in substitutional alloys has been extensively developed in recent years, notably through the use of the coherent-potential

approximation[2] (CPA) and related approaches. However, the CPA has proven to be difficult to generalize to any significant extent, at least in forms suitable for computation on real systems. Desirable generalizations are the inclusion of disorder that is not site-diagonal (force-constant disorder in the phonon problem) and the treatment of local environment effects that tend to produce structure in densities of states or spectral functions. The latter effects, which we refer to interchangeably as local environment effects, or cluster effects, occur even in alloys without any short-range order, and arise essentially because the near-neighbor environment varies from site to site in a nondilute alloy. Such effects are neglected in theories such as the CPA, which consider only the scattering properties of an average single site (single-site approximation). Cluster effects are expected to be most pronounced for concentrations where localized states are acquiring propagating characteristics.

Force-constant disorder can be included[3,4] in the single-site CPA with certain restrictions. Two calculations of this type have been carried out for comparison with our $Rb_{1-c}K_c$ results, by Mostoller and Kaplan[5] and by Grünewald and Scharnberg.[6] We discuss their results in Sec. IV. The treatment of local environment effects is more difficult, and it is doubtful that calculations in three dimensions based on a theory that includes such effects will be carried out in the near future.[7] Another approach applicable to the dynamics of

alloys, and of disordered and anharmonic systems
in general, lies in the use of computer simulation.
Although earlier numerical methods yielded only
densities of states, recent studies of the molecu-
lar-dynamics type have shown that the coherent
neutron scattering law $S(\vec{Q}, \omega)$ can be extracted
from a sufficiently detailed calculation. Recently,
such computer simulation studies have been per-
formed on Rb$_{1-c}$K$_c$ by Jacucci, Klein, and Taylor,[8]
and we shall discuss their calculations in Sec. IV.
It is to be expected that local environment effects
are more accurately treated by computer simula-
tion than by CPA-type theories, but difficulties
could conceivably arise because of the relatively
small number of particles that can be used in the
calculation.

A number of neutron experiments on the phonon
spectra of alloys have been reported. These in-
clude coherent scattering studies on localized
modes in Cu$_{1-c}$Al$_c$,[9] Ge$_{1-c}$Si$_c$,[10] and K$_{1-c}$(NH$_4$)$_c$Cl,[11]
and similar experiments on resonance modes as-
sociated with the heavy-atom constituents in[12]
Cu$_{1-c}$Au$_c$ and Cr$_{1-c}$W$_c$.[13] These studies and related
theoretical analyses indicate that with the excep-
tion of Ge$_{1-c}$Si$_c$, force-constant disorder caused
by the alloying must be considered simultaneously
with the mass disorder in order to obtain quantita-
tive agreement between theory and experiment.
Also, it was generally found[9,14] to be necessary
to consider the changes in phonon frequencies
caused by expansion or contraction of the lattice
on alloying separately from the disorder effects.
A summary of efforts to analyze the experiments,
with force-constant changes included, is given by
Mostoller and Kaplan in the introduction of Ref.
5.

In the experiments described in Refs. 9–13, we
have $c \leqslant 0.10$, so that a low-concentration theory
is applicable and it is not absolutely necessary
to employ the CPA. Experiments for higher-con-
centration alloys have been carried out on
Ni$_{0.55}$Pd$_{0.45}$,[15] and more recently on Bi$_{1-c}$Sb$_c$ al-
loys[16] with $c = 0.12$ and 0.17. The data on
Ni$_{0.55}$Pd$_{0.45}$ were compared with the mass-defect
CPA with qualitative success, but it was clear that
force-constant disorder would have to be included
to obtain quantitative agreement with experiment.
The Bi$_{1-c}$Sb$_c$ results were compared with both
CPA and ATA (average-t-matrix approximation)
calculations.

Force-constant disorder and lattice expansion
must also be taken into account in order to de-
scribe the present results on Rb$_{1-c}$K$_c$ alloys. How-
ever, there are two reasons which make this sys-
tem particularly attractive for detailed calcula-
tions. First, because of the simple nature of the
phase diagram of the Rb-K system, large homo-

geneous alloy crystals can be grown without sig-
nificant long- or short-range order. Second, the
alkali metals are the best understood of all metals
with respect to their lattice dynamics. Force-
constant changes for these alloys can be calculated
by microscopic theory in a satisfactory manner,
starting from the properties of the pure metals,
and need not be treated as fitting parameters.
Rubidium and potassium both have favorable neu-
tron properties, and the lattice dynamics of both
have been thoroughly investigated.[17,18]

II. EXPERIMENT

A. Crystal growth

The phase diagram[19] for Rb$_{1-c}$K$_c$ shows a con-
tinuous series of solid solutions with solidus and
liquidus temperatures differing by less than 0.2 K
for $c < 0.4$, implying that in this concentration
range homogeneous single crystals can be ob-
tained by the Bridgman method. We know of no
data available on the phase diagram of Rb-K below
300 K, but we think that phase separation is un-
likely to occur at lower temperatures. Theoreti-
cal considerations based on the method of crystal
growth lead us to believe that the concentration
spread Δc in any of our samples does not exceed
5% of the mean concentration c.

The crystals were grown in a large glove box,
continuously flushed with dry nitrogen gas, using
the modified Bridgman technique first employed
on the alkali metals by Daniels.[20] The crystal-
growth apparatus consisted essentially of a stain-
less-steel crucible with a 2.5-cm i.d. surrounded
by a removable gradient-wound heater unit that
produced, at the start of the growth process, a
temperature difference of about 20°C between the
bottom and top of the crucible. The total inside
height of the crucible was about 20 cm, including
a conical bottom section of about 5-cm height
which could be unscrewed to permit removal of the
boule.

The alkali metals, obtained from MSA Research
Corporation, Evans City, Pennsylvania in 50-g
glass ampoules with stated purities of 99.9$^+$%,
were first melted in the ampoule and then trans-
ferred in a heated pipette to the heated crucible
until the desired mass had been introduced. The
melt was then stirred for a few minutes and final-
ly cooled over a period of 6–12 h using an elec-
trically driven Variac.

When completely cold, the crucible was sealed
at the top and removed from the glove box. The
boule was examined while still in its crucible
on a two-axis neutron diffractometer at the Ar-
gonne CP5 research reactor. Single crystals thus
obtained were characterized for orientation and

mosaic spread. Unsatisfactory boules were re-
turned to the glove box, remelted, and a new at-
tempt then made to grow a single crystal. Satis-
factory boules were returned to the glove box,
removed from the crucible, and cut to size with a
continuously running cotton-string saw. A mix-
ture of 50% methanol in water proved to be the
most suitable cutting fluid. A typical cut through
a 2.5-cm boule took 30–60 min. Crystals were
finally etched to size in a mixture of 1–2-vol.%
butanol in xylene, allowed to form a thin protec-
tive oxide layer, and placed in a thin-walled (0.1
cm) aluminum container equipped with indium
seals.

The four crystals used in the experiment were
further characterized using a two-axis neutron
diffractometer at the McMaster University re-
search reactor in Hamilton, Ontario. The mea-
sured lattice constants are given in Table I along
with other sample characteristics. The crystals
were of comparable quality, exhibiting mosaic
widths from 0.3° to 0.6° full width at half maxi-
mum (FWHM). The lattice constants fall very
close to a linear interpolation between pure Rb
and pure K. Since θ–2θ scans at large θ are quite
sensitive to variations in the lattice parameter,
they are also sensitive to the related variation in
alloy composition. No inhomogeneity in our crys-
tals could be detected under conditions of quite
high resolution.

B. Neutron scattering

The inelastic scattering measurements of the
phonon spectra were carried out on a variable-
incident-energy triple-axis spectrometer at the
high flux isotope reactor in Oak Ridge. Almost
all data were taken with the samples held at 10 K
by an Air Products helium-gas cycle refrigerator.
A fixed scattered-neutron energy $E' = 2.8$ THz
was used to make nearly all the high-resolution
measurements on the local-mode region, while
most of the lower-resolution data on the band
modes were taken with $E' = 3.3$ THz. Beryllium
monochromator and analyzer crystals were used
throughout the course of the experiment, with
pyrolitic graphite filters in the scattered-beam

path to reduce contaminant neutron processes.
The data were always taken in constant-$\vec{Q}$ scans,
with $\vec{Q} = (2\pi/a)(2+\zeta, 2+\zeta, 0)$ for $[\zeta\zeta 0]$ longitudinal
vibrations, and $\vec{Q} = (2\pi/a)(2, 2, \zeta)$ for $[00\zeta]$ trans-
verse vibrations.

III. RESULTS

The main features of the experimentally ob-
served phonon spectra are illustrated in the scans
shown in Fig. 1 and in the dispersion curves plot-
ted in Fig. 2. The small mass of a K atom rela-
tive to an Rb atom causes most of the phonon
spectral density for the potassium sites to appear
in a high-frequency local-mode peak above the
host (Rb) lattice frequencies. The local-mode fre-
quencies ν_l show a marked increase with concen-
tration. They are relatively dispersionless, but
not completely so. The local-mode intensities de-
pend strongly on both wave vector and concentra-
tion.

In Fig. 1 is shown the scattering from zone-
boundary longitudinal vibrations in the $[\zeta\zeta 0]$ direc-
tion. As expected from theory,[21] and as noted in
previous[9-11] neutron scattering experiments, the
scattering from the local mode is strongest at such
a point in reciprocal space, where the host (Rb)
crystal phonon frequency $\nu_0(j\vec{q})$ attains its maxi-
mum value.[15] The scattering varies roughly as
$[\nu_l^2 - \nu_0^2(j\vec{q})]^{-2}$, and thus decreases rapidly away
from this wave vector. The only values of $(j\vec{q})$ for
which the local-mode scattering is comparably
strong are those for transverse vibrations near the
H point ($[00\zeta]$ zone boundary), where $\nu_0(j\vec{q})$ again
attains a value close to the maximum. This local-
ization of the impurity mode scattering in $\vec{Q}$ space,
observed in the previous neutron scattering ex-
periments[9,10] on $Cu_{1-c}Al_c$ and $Ge_{1-c}Si_c$ alloys, was
interpreted as arising from localization in real
space, the vibrational amplitudes of the impurity
mode having a range inversely related to the ex-
tent of the intensity distribution in $\vec{Q}$ space.

The increase in the local-mode frequency and
width with concentration is illustrated in Fig. 1.
For $c = 0.06$, the 1.69-THz local-mode peak is
about half as intense as the 1.50-THz band-mode
peak, and little or no broadening above resolution

TABLE I. Characteristics of $Rb_{1-c}K_c$ samples.

K (at.%)	0	6.0	18.1	29.1
Height (cm)	7.4	7.9	8.0	5.3
Diameter (cm)	2.5	2.5	2.5	2.5
Lattice constant (Å) at 296 K	5.702 ± 0.001	5.678 ± 0.001	5.636 ± 0.001	5.599 ± 0.001

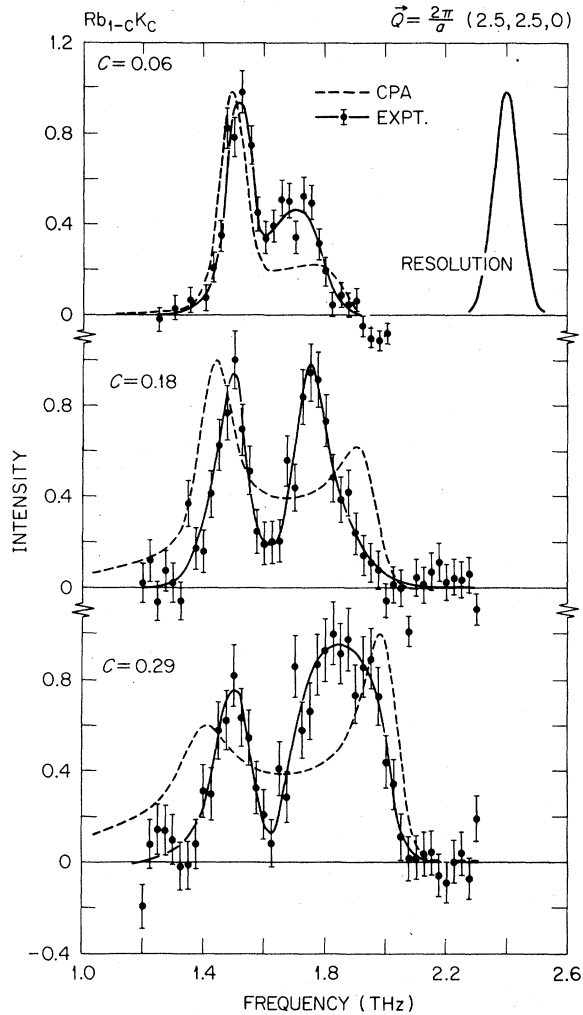Rb$_{1-c}$K$_c$ $\vec{Q} = \frac{2\pi}{a}$ (2.5, 2.5, 0)

FIG. 1. Constant-$\vec{Q}$ scans for [$\zeta\zeta 0$] longitudinal zone-boundary vibrations, showing band-mode peaks (1.5 THz) and local modes (1.7–1.9 THz). An almost flat background has been subtracted from each scan. Dashed lines are CPA calculations with mass disorder only. Solid lines are guides to the eye. Curves and data points are normalized to a maximum value of 1.0.

FIG. 2. Dispersion curves for [$\zeta\zeta 0$] longitudinal vibrations, and the $\vec{Q}$ dependence of the local-mode strength f (inset). Crosses (+) are data points for $c = 0.06$ measured with poorer resolution.

is apparent. For $c = 0.18$, the local-mode peak has risen to 1.75 THz and is now well resolved from the band mode, but is still not broadened much above resolution (0.1 THz FWHM), although it may have a high-frequency tail. For $c = 0.29$, the local mode dominates in intensity and has become strongly broadened to about 0.3 THz FWHM. The band-mode frequency is the same for all three concentrations. The dashed lines in Fig. 1 are CPA calculations that will be discussed in Sec. IV.

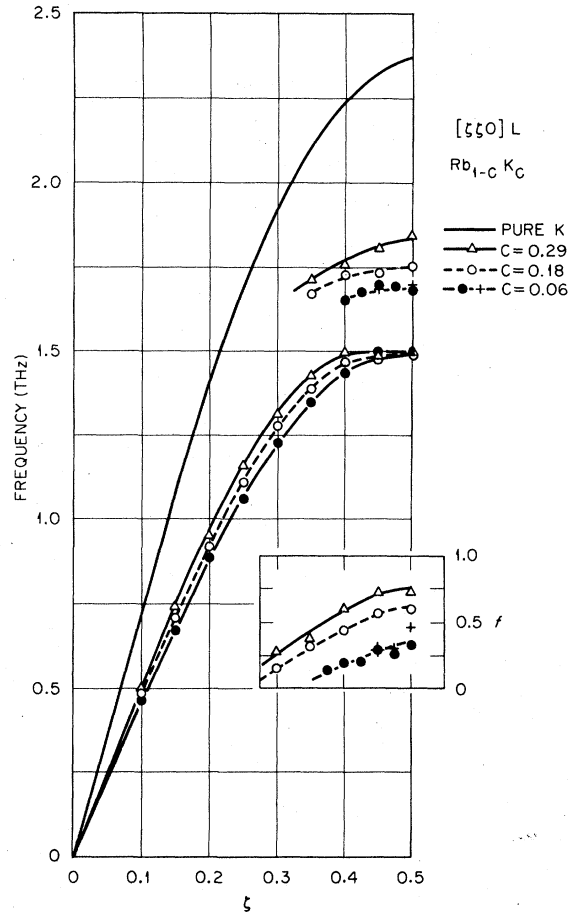Dispersion curves for [$\zeta\zeta 0$] longitudinal vibrations are shown in Fig. 2. For pure Rb, the dispersion curve is indistinguishable from that of Rb$_{0.94}$K$_{0.06}$. From this figure, one can see how the dispersion curve for pure K evolves from those of the alloys as c is increased. The band modes rise in frequency at lower wave vectors, but not at the zone-boundary point $\zeta = 0.5$. As the local mode rises in frequency and increases in strength, the band mode decreases in strength, the integrated intensity over both peaks at the same wave-vector transfer $\vec{Q}$ remaining nearly constant. In the inset of Fig. 2, f is the fraction of the integrated intensity in a constant-$\vec{Q}$ scan contained in the local-mode peak, corrected for the factor $[n(\nu) + 1]/\nu$ in the cross section. Thus f corresponds roughly to a fractional spectral weight, diminished to some extent by the fact that the scattering length of K ($b = 0.37 \times 10^{-12}$ cm) is smaller than that of Rb ($b = 0.71 \times 10^{-12}$ cm). The wave-vector dependence of the local-mode intensity is similar

for the three concentrations. The frequencies, however, appear to show more dispersion at c $= 0.29$ than at lower c, indicating that the local mode is starting to acquire a propagating character.

Scattered neutron distributions for the $[\zeta\zeta 0]$ longitudinal modes in $Rb_{0.71}K_{0.29}$ are shown in Fig. 3. Here one can see how the intensity transfers from the high-frequency local mode to the low-frequency mode as one goes away from the zone boundary. Molecular-dynamics calculations[8] indicate that these modes are associated with K and Rb motions, respectively. The dispersion in the local-mode frequency is clearly noticeable.

Similar data have been taken for the $[00\zeta]T$ branch, for which the local mode acquires significant intensity near the H point $\vec{Q} = (2\pi/a)(2,2,1)$. In Fig. 4 we compare the frequency shifts $\nu(Rb_{1-c}K_c) - \nu(Rb)$ for the three concentrations. The shifts are found to be the same for the $[00\zeta]T$ branch as for the $[\zeta\zeta 0]L$ branch, within experimental error, when plotted against $\nu(Rb)$. However, when a similar plot (Fig. 5) is made for the local-mode intensity f, $[00\zeta]T$ is found to be the same as $[\zeta\zeta 0]L$ for $c = 0.18$, but not for $c = 0.29$. The reason for plotting f and the shifts against $\nu(Rb)$ has to do with the predictions of theories for disordered alloys, as discussed in Sec. IV.

Since the anharmonic shifts and widths at room temperature are comparable to the disorder-induced alloy effects, we have checked to see if the local mode in $Rb_{0.94}K_{0.06}$ shows any unusual behavior with changing temperature; it does not, as shown in Fig. 6. At the higher temperatures, the peaks are broadened and shift slightly downward on top of a rising background, but no change in the structure of the scans otherwise occurs. There is a noticeable broadening of the peaks even at 85 K, leading us to choose 10 K as the sample temperature for most of our measurements.

IV. DISCUSSION

One motivation for this experiment was to provide neutron scattering data that would require a description beyond the single-site CPA for phonons. To a large extent, this purpose has been fulfilled, since there are strong indications that local environment effects are present. However, the interpretation is not completely unambiguous, since force-constant disorder, and the extent to which it can be included in the CPA, must be considered simultaneously with local environment effects.

Because we have studied three alloys in the present experiment, increasing c to the rather large value of 0.29, one feature is evident from
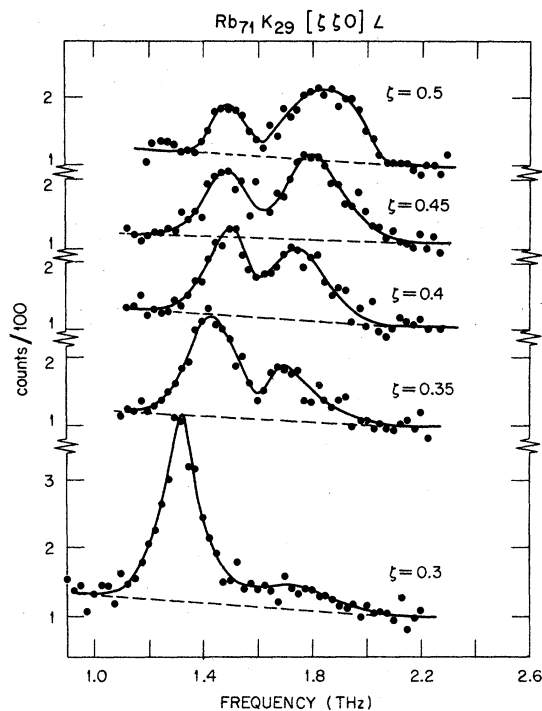

FIG. 3. Constant-$\vec{Q}$ scans for $[\zeta\zeta 0]$ longitudinal modes in $Rb_{0.71}K_{0.29}$.

our results which is not obvious from previous experiments[9,10] on $Cu_{1-c}Al_c$ and $Ge_{1-c}Si_c$. This concerns the evolution of the local mode as c is increased. From our data, it is clear that the lo-

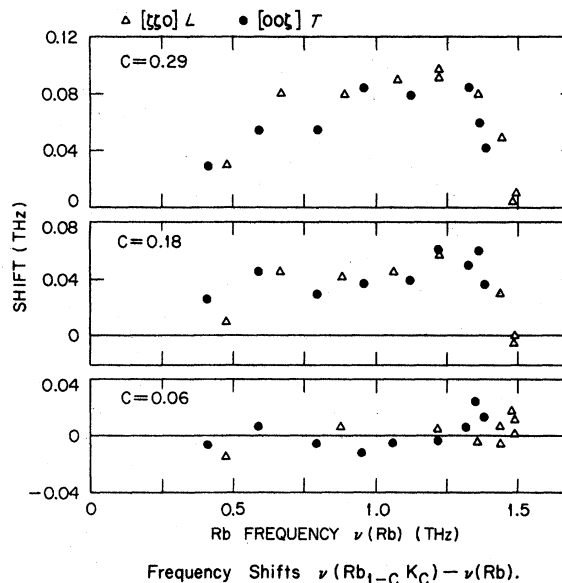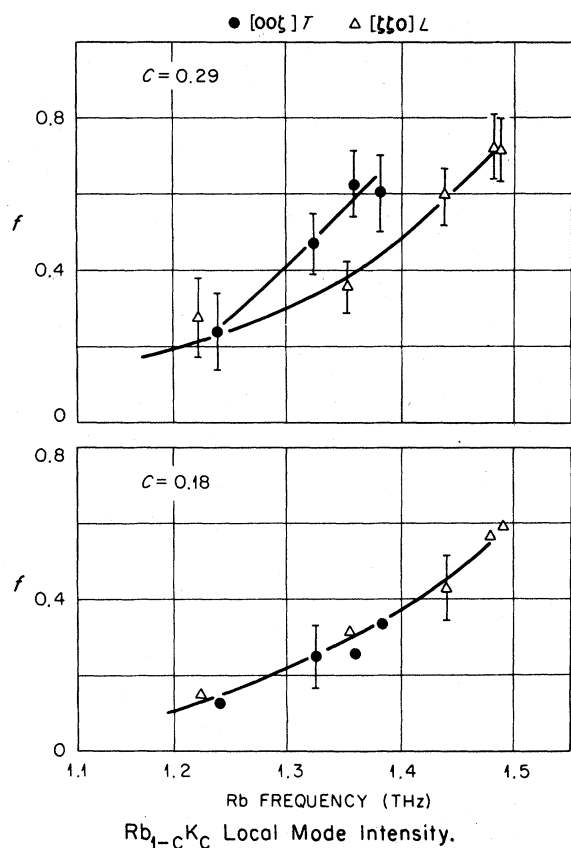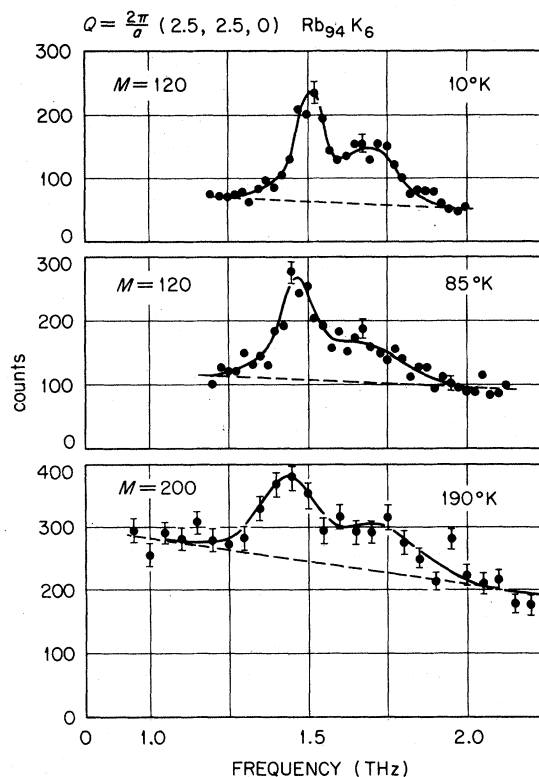Frequency Shifts $\nu(Rb_{1-c}K_c) - \nu(Rb)$.

FIG. 4. Frequency shifts of band modes for the two measured branches.

FIG. 5. Local-mode strength f vs host frequency.

FIG. 6. Temperature dependence of longitudinal [$\zeta\zeta 0$] zone-boundary scan for $c = 0.06$. M is proportional to the counting time.

cal mode increases in intensity and rises in energy, eventually becoming the band mode near the zone boundary. Meanwhile, along any branch that reaches a sufficiently high frequency, the value of $|\vec{q}|$ for which the local mode and band mode are equal in intensity will decrease as c is increased. Since a smaller $|\vec{q}|$ implies a lower frequency, the gap region between local mode and host mode will drop in frequency as intensity is eroded away from the top of the host-mode spectrum. Eventually, at still higher c, the gap region will evolve into an in-band resonance mode as the "host" becomes the minority constituent of the alloy. A similar kind of behavior was predicted by Taylor (Fig. 8 of Ref. 2) in his original paper on the CPA for a mass ratio 3.1 : 1.

Many of the features observed in this experiment can be understood at least qualitatively in terms of low-concentration theories[21] of Elliott and Maradudin and of Elliott and Taylor, which were the direct predecessors of the phonon CPA of Taylor.[2] The experiments on Cu$_{1-c}$Al$_c$ and Ge$_{1-c}$Si$_c$ were analyzed quite successfully in terms of the low-c theory. The CPA has been applied to

Ge$_{1-c}$Si$_c$ and gives similar results.[22] These theoretical analyses treat mass disorder only, and force-constant disorder must be included[23] to obtain a closer match with experiments on Cu$_{1-c}$Al$_c$ and (NH$_4$)$_c$K$_{1-c}$Cl, although the case of Ge$_{1-c}$Si$_c$ does not seem to require consideration of force-constant disorder.

Single-site approximations that treat mass disorder only give a phonon self-energy which depends only on the frequency $\nu(j\vec{q})$ of the host lattice and not on $(j\vec{q})$ explicitly. Inclusion of force-constant changes generally will yield an explicitly $(j\vec{q})$-dependent self-energy, though apparently not always, as Grüewald's theory,[4] discussed below, is an exception. A theory that fully includes cluster effects would also produce a $(j\vec{q})$-dependent self-energy. In Figs. 4 and 5 the band-mode frequencies and local-mode intensities are plotted against $\nu(j\vec{q})$ to assess whether explicit $(j\vec{q})$ dependence is needed for Rb$_{1-c}$K$_c$. The band-mode shifts do not seem to require such dependence at all, since [00ζ]T and [$\zeta\zeta 0$]L give the same result within experimental error. However, the local-mode intensities suggest that some $(j\vec{q})$ dependence is needed for $c = 0.29$, where [00ζ]T and [$\zeta\zeta 0$]L points

lie on different curves, but not for $c = 0.18$, where they lie on the same curve. Since the relative force-constant changes $[\phi(\text{Rb-Rb}) - \phi(\text{Rb-K})]/\phi(\text{Rb-Rb})$ are not likely to be very different for the two alloys, this is an indication, although a rather weak one because of limited data, that cluster effects are present, since these are expected to be more important for $c = 0.29$. A much stronger indication that cluster effects are present is the large width of the local mode at N for $c = 0.29$, which can be interpreted as a distribution of local-mode frequencies arising from the highly variable local environments of the K atoms. This viewpoint can be more convincingly argued by comparison with calculated scattering cross sections.

The dashed lines in Fig. 1 are CPA cross sections assuming mass changes only. The difference in scattering lengths of Rb and K has been taken into account,[2] and a resolution width of 0.1 THz FWHM has been folded into these and all other calculated cross sections that we shall discuss. The calculated curves and experimental data points have been normalized so that the maximum values in a scan are set at 1.0 on the vertical scale. The solid lines are guides to the eye drawn through the data points. The CPA calculations show qualitative similarity to the data, but there is much room for improvement. Even at $c = 0.06$, the observed local-mode frequency is lower than the prediction of the mass-defect CPA. This is most likely due to force-constant changes. For $c = 0.18$ and 0.29, the minima between host and local mode are too shallow and the peaks are too far apart. It is probable that much of the disagreement for the higher concentrations is due to the nature of the approximation in the single-site CPA, and is not just the result of force-constant disorder.

The latter contention is borne out by two detailed theoretical analyses of our data, in which force-constant changes are considered within the single-site CPA and neutron scattering cross sections are calculated. Kaplan and Mostoller have worked out a theory[3] in which force-constant changes are included subject to the constraint that they superimpose linearly. In practice this means that the Rb-K force constants are assumed to be the average of Rb-Rb and K-K force constants. In applying the theory to $\text{Rb}_{1-c}\text{K}_c$, Mostoller and Kaplan (MK) find[5] that it is possible to obtain some improvement over the mass-defect CPA by making a 13% reduction in the nearest-neighbor radial Rb-K force constants, but most of the discrepancy at $c = 0.18$ and 0.29 still remains when this is done. Representative of their results are the calculations for the zone-boundary modes in $\text{Rb}_{0.71}\text{K}_{0.29}$ shown as the dot-dashed lines in Fig.

7. For the N point $(2.5, 2.5, 0)$ the peak positions are improved, but the minimum between the two peaks has been wiped out and the large width of the local mode is not reproduced. The agreement is considerably worse for the H point $(2, 2, 1)$ and for the $[00\zeta]T$ local modes in general. The local-mode frequency has been lowered in frequency so much that it has merged into a single peak with the host mode. However, for both $[00\zeta]T$ and $[\zeta\zeta 0]L$ branches, the frequencies of host-mode phonons away from zone-boundary regions are very accurately prdicted.[5]

Grünewald and Scharnberg[6] (GS) have also carried out an analysis of our data based on a force-constant-CPA theory of Grünewald.[4] Their results, which always give correct peak positions for the local mode, are much better than those of MK for $[00\zeta]T$ vibrations and slightly better for $[\zeta\zeta 0]L$ modes, as shown in Fig. 7. The minima between local and host mode are still too shallow,

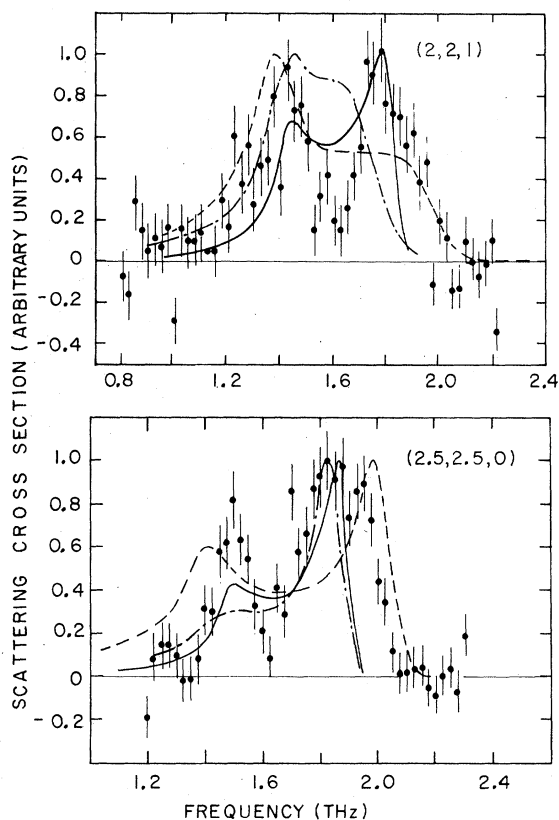

FIG. 7. Comparison of calculations for zone-boundary vibrations in $\text{Rb}_{0.71}\text{K}_{0.29}$: mass defect CPA(---); force constant CPA of Mostoller and Kaplan(-·-·); force constant CPA of Grünewald and Scharnberg (——). Curves and data points are normalized to a maximum value of 1.0.
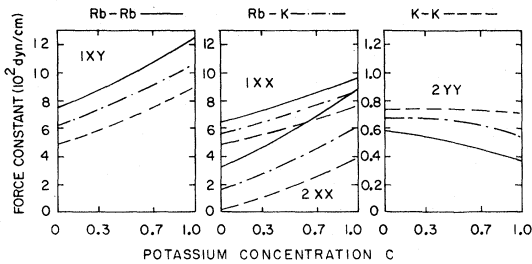
FIG. 8. Force constants in Rb-K alloys derived by Grünewald and Scharnberg (Ref. 6) from Ashcroft pseudopotentials. The notation $(1XX, 1XY, \cdots)$ is described in Ref. 17.

however, and the distributions do not extend to a high enough frequency. The method of GS, computationally much simpler than that of MK, gives a self-energy that depends only on the host-lattice frequency $\nu(j\vec{q})$, and not explicitly on $(j\vec{q})$. Thus it may not be suitable for describing results on phonon shifts and widths in the Cu-Au, Cr-W, or Ni-Pd systems, each of which shows a $(j\vec{q})$-dependent pattern. In their calculation, GS assume that Rb-K force constants are the geometric mean of Rb-Rb and K-K force constants, although this restriction does not appear to be strictly necessary in their formalism. The force constants used by GS were obtained from microscopic calculations based on pseudopotential theory, i.e., essentially a first-principles approach to calculating force-constant changes. They obtain Rb-Rb, Rb-K, and K-K force constants as functions of c (Fig. 8), and the arithmetic and geometric mean approximations of MK and GS, respectively, appear to be well justified. Thus for this particular alloy system it is unlikely that the approximations necessary to include force-constant changes in the CPA are responsible for the remaining disagreement with experiment. MK may have made an unfortunate choice in using virtual-crystal force constants for the host lattice. Referring to Fig. 8, the choice of MK corresponds to representing the host-crystal (Rb-Rb) force constants as a straight line joining the leftmost point on the Rb-Rb curves of GS to the rightmost point on the K-K curves. Thus the host force constants may be consistently underestimated by MK, possibly explaining the better overall agreement with experiment achieved by GS.[24]

The common faults shared by the results of GS and MK are that the minima between local- and host-mode peaks are always too shallow, and the experimental local modes extend to higher frequencies than the calculated distributions. The first of these characteristics strongly suggests the importance of local environment effects, re-

sembling the deficiencies of numerous CPA calculations when compared with exact numerical results. For low concentrations, the CPA often seems to give[25] an impurity band structure that is too "washed out," presumably because of the mean-field nature of the CPA. The self-consistent calculation approximates the environment of each impurity by the imperfect crystal itself. However, at low c the environment of an average impurity looks more like a perfect crystal because few other impurities are nearby. At higher concentrations $(c \sim 0.3)$ the local environment of an impurity is highly variable, with stronger effects on local modes than on band modes. This is the poorest regime of validity for the CPA. At still higher c, where the local mode no longer exists but only an in-band resonance is present, the CPA regains validity. To generalize the CPA to include local environment effects is certainly very difficult. A number of attempts have been made,[26] but to the authors' knowledge no solution valid for a full range of alloy parameters (mass difference, force-constant differences, or analogous electronic or magnetic parameters) has been found.

On the other hand, computer simulation of the dynamics of aggregates of atoms interacting through specific pair potentials provides a way to include local environment effects. Calculations of the molecular-dynamics (MD) type[27] have recently been developed that allow evaluation of the coherent scattering law $S(\vec{Q}, \omega)$ for disordered and anharmonic systems.[28] Jacucci, Klein, and Taylor have recently carried out MD calculations[8] for comparison with some of our results on Rb$_{0.71}$K$_{0.29}$. In Fig. 9 we show such a comparison for two zone-boundary phonons. The MD calculations shown in Fig. 9 correspond to the heavy curves in Figs. 7 and 9 of Ref. 8. The MD calculations correspond to a temperature of 80 K, whereas the neutron results were obtained at 10 K. Nevertheless, the agreement with experiment is rather good, improving on the CPA results in two important respects. The local mode in the MD calculations now has a substantial width, in good agreement with our neutron data for $\vec{Q} = (2, 2, 1)$, and in reasonably good agreement for $\vec{Q} = (2.5, 2.5, 0)$. Also, the deep minimum between the two peaks is now well reproduced for $\vec{Q} = (2, 2, 1)$. The only major discrepancy between calculation and experiment is the relative strength of host- and local-mode peaks. The host mode is too weak for $\vec{Q} = (2, 2, 1)$ and much too weak for $\vec{Q} = (2.5, 2.5, 0)$. In other respects, however, the agreement with experiment is very good, particularly for peak positions at all wave vectors, as shown in Fig. 11 of Ref. 8 by Jacucci, Klein, and Taylor. The natural inclusion of local
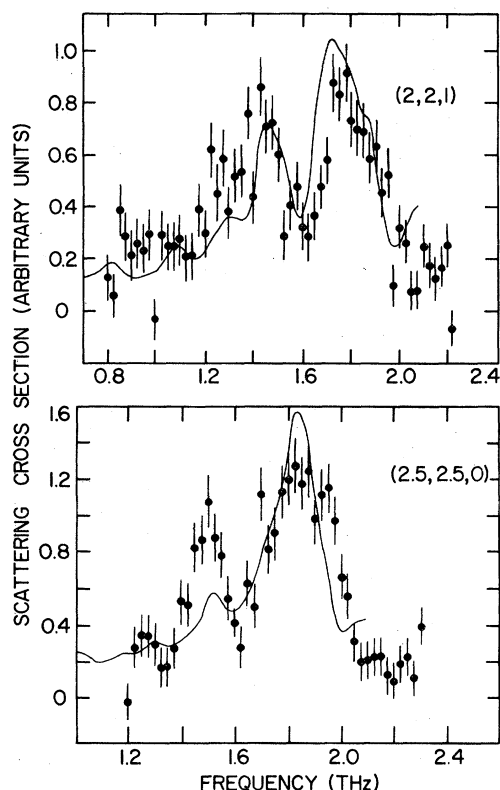
FIG. 9. Comparison of experiment with molecular-dynamics calculations (solid lines) of Jacucci, Klein, and Taylor (Ref. 8) for zone-boundary modes in $Rb_{0.71}K_{0.29}$. The experimental data have been adjusted with respect to background level and magnitude to provide a good overall match with the MD lines.

environment effects in the MD calculations seems to have produced a substantial improvement over the CPA calculations.

In our opinion, it would be worthwhile to pursue further investigations on Rb-K and other alloy systems using neutron scattering and molecular dynamics in a combined approach. In particular, if in a binary alloy $A_{1-c}B_c$, isotopes with markedly different scatterings lengths for at least one of A or B are available, then it may be possible to extract the partial scattering functions describing AA, AB, and BB correlated motions.

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