Vibrations of a mixed crystal: Neutron scattering from $Ni_{55}Pd_{45}$

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The crystal dynamics of an alloy with a large amount of mass disorder (Ni and Pd have masses 58.7 and 106.5 amu, respectively) have been investigated by inelastic neutron scattering. A triple-axis spectrometer was used to measure the phonon dispersion curves and widths in a crystal of the fcc random alloy $Ni_{55}Pd_{45}$. Significant broadening was observed in each branch for neutron groups corresponding to phonons of large wave vector. For transverse modes, many of the widths are large and indicate behavior characteristic of resonance modes. Neutron groups for [111] transverse vibrations at the zone boundary had the largest widths (2.1 THz, compared with a mean frequency of 3.3 THz). The widths of the longitudinal modes are generally smaller than those of transverse modes, and no definite indications of resonance behavior are apparent. The results are compared with the predictions of several theories, notably the coherent-potential approximation with some qualitative success. The form of the discrepancy between theory and experiment, and the similarity of the results to those of an experiment on crystals containing relatively dilute concentrations of Au in Cu, suggest the need to consider force-constant changes as well as mass disorder. Some new measurements for Cu(Au) are also reported.

I. INTRODUCTION

A substantial amount of research has been carried out over the past few years on the nature of elementary excitations in disordered alloys. Many aspects of the lattice vibrational, magnetic, and electronic excitations in such systems have been intensively studied in interrelated theoretical and experimental investigations. The phonon problem is perhaps the best understood and many qualitative features can be visualized in very simple terms. An atom that is sufficiently light or tightly bound in a matrix of heavy atoms will vibrate in a high-frequency local mode, spatially localized about the light atom. An atom that is sufficiently heavy or weakly bound will vibrate in a low-frequency resonance mode, or "quasilocalized" mode. The lack of exact translational symmetry in a disordered alloy must give finite energy widths, or equivalently, limited lifetimes, to the phonons, but these widths must be small if the difference between the masses and chemical properties of the constituents are small. On the other hand, if the differences are large enough, the vibrational spectrum can split into two or more distinct bands, a condition whose occurrence will depend on the concentrations of light and heavy atoms.

Phonons are not only conceptually the simplest type of elementary excitation but are also the most readily accessible to detailed experiment. The neutron scattering technique, which has provided extremely detailed information about lattice vibrations in perfect crystals has, in recent years, been turned to the study of imperfect-crystal dynamics. Here and in the following, the term "imperfect crystal" will be used primarily to refer to substitutionally disordered binary alloys. Some of the neutron scattering experiments have been involved with the study of local modes or resonance modes associated with a few atomic percent of atoms that are considerably lighter than or heavier than the atoms of the host lattice. Results[1–5] have been obtained on single crystals of Cu(Au), Cr(W), Cu(Al), Cu(Si), and Ge(Si). A few other alloy systems have been investigated in polycrystalline form.

At the higher concentrations involved in the preceding experiments, up to 9 at.%, the vibrations of an impurity atom are somewhat affected by the presence of adjacent impurities. Such concentration effects are of major interest in this type of experiment. Along this line, the question arises as to what are the characteristics of the excitations when the impurity concentration is very high, so that neither light nor heavy atoms can be considered to be the "host" or "impurity" constituent. The problem of describing the vibrations for a high-concentration imperfect crystal is much more difficult than for low impurity concentrations, and all theories to date involve questionable assumptions.

Experimentally, the problem is also difficult to approach. The optical methods which have given such detailed information about impurity vibrations for very low concentrations reveal much less information for very high concentrations. Perhaps the only spectroscopic technique that is not severely restricted in principle in its application to this problem is inelastic neutron scattering. Coherent inelastic neutron scattering can give the frequencies and frequency widths of the phonons as functions of wave vector, and is not restricted to any particular class of materials. Especially impor-

TABLE I. Properties of Ni and Pd.

	Ni	Pd
Atomic number	28	46
Atomic mass (amu)	58.71	106.4
Free-atom ground state	$3d^8 4s^2$	$4d^{10}$
Lattice constant (Ref. 14) (fcc) at room temperature (Å)	3.524	3.8904
Thermal neutron cross sections (Ref. 15) (b):		
σ_{coh}	13.2 ± 0.2	5.0 ± 0.3
σ_{incoh}	4.8 ± 0.3	...
σ_{absorp}	4.8 ± 0.2	8.0 ± 1.5
Elastic constants (Refs. 16 and 17) at 296°K (10^{12} dyn/cm):		
C_{11}	2.46	2.270
C_{12}	1.50	1.759
C_{44}	1.22	0.717
Melting temperature (°C)	1455	1549.4

tant is its applicability to metals, and concurrently to the monatomic systems which will naturally constitute the most tractable theoretical cases. It thus appears that more extensive application of coherent inelastic neutron scattering to disorder effects in high-concentration random alloys is overdue.

Besides the work that is reported in this paper, part of which has appeared elsewhere[6] in preliminary form, there has been to our knowledge only one other experiment by coherent scattering on a high-concentration imperfect crystal, a study[7] of some branches in KBr : RbBr mixed crystals containing 22 and 45-mole% RbBr. On the whole, little evidence of the influence of the mass disorder on the frequencies or widths of the phonons was seen in this experiment, although effects characteristic of a resonance mode were observed in the [111]LA branch. The primary conclusion to be drawn from the KBr : RbBr experiment is that phonons remain a good description of crystal dynamics even in the presence of substantial mass disorder. It should be noted, however, that such a system has two atoms per unit cell, and even at a concentration of 45-mole% RbBr only 22.5% of the atoms are Rb, so that the amount of disorder is not so very large, particularly since the nearest neighbors of a rubidium atom are always bromine atoms. The calculational difficulties associated with diatomic or polyatomic disordered crystals are also considerable. Even models for the host or reference lattice which give reliable frequency distributions and eigenvectors are much more difficult to produce than for simple monatomic crystals. Certainly it is very desirable to study the vibrations in a high-concentration imperfect crystal with a bcc or fcc structure, in order to maximize the amount of disorder, and, at the same time, to retain the possibility of adequately interpreting the results.

Disorder effects have been studied primarily in alloys in which the atomic masses of the constituents differ by factors of 2 or 3. In alloys (assumed to be monatomic) in which the component elements are neighbors or near neighbors in the Periodic Table, the masses differ by only a few percent, much too small[8] an amount to produce disorder broadening observable by neutron scattering. However, one might expect significant disorder broadening to arise from force-constant disorder, particularly since the components in such alloys will have very different electronic and chemical properties. Experiments[8–12] by coherent inelastic neutron scattering have been carried out on Bi-Pb-Tl, Nb-Mo, Fe-Ni, Cu-Zn, and Cu-Ni alloys, sometimes over wide ranges of composition. Little or no phonon broadening was noted in most cases, though there were exceptions.[8] On the whole, it can be fairly stated that the effects from disorder in these alloys are surprisingly small. One should therefore clearly distinguish between the studies whose primary purpose is to determine the effect of the average electronic structure on the phonon dispersion curves, and experiments on mass-disordered alloys, which are mainly intended to reveal information about disorder effects.

II. EXPERIMENT

A. Choice of the Ni-Pd system

The mass ratio of Pd to Ni ($M_{Pd}/M_{Ni} = 1.812$) is certainly not small, but is not as large as that of Au to Cu ($M_{Au}/M_{Cu} = 3.100$). This may make a high-concentration imperfect crystal of Ni and Pd a more approachable theoretical problem than a high-concentration alloy with a very large mass ratio. A neutron scattering experiment[13] on polycrystalline alloys of Pd–5-at.% Ni and Pd–10-at.% Ni gives evidence that Ni has a local mode in a Pd host, as one would expect from mass-defect theory. Other properties of the Ni-Pd system make it a particularly favorable case for an experiment by coherent inelastic neutron scattering.

We shall often make comparisons with the Cu(Au) systems, which has a number of relevant similarities to the Ni-Pd system. Most importantly, the phonon spectra of relatively dilute Cu(Au) alloys, as revealed by neutron scattering experiments,[1] bear strong similarities to the results of the present experiment on Ni-Pd.

Ni and Pd, which come from the same column of the Periodic Table, have rather complicated electronic structures which are similar to each other, but are not as much alike as are the noble metals. Some properties of Ni and Pd relevant to our experiment are listed in Table I. The lattice parameters differ by about 11% (compared with about 10% for Cu and Au) and the melting temperatures differ by about 6% (compared with about 2% for Cu and

TABLE II. Force constants of Pd and Ni, in units of dyn/cm, as derived from neutron measurements (Refs. 19 and 20) at room temperature. Also shown are the force constants of the $Ni_{55}Pd_{45}$ mean-crystal model used in the calculations discussed in the text. These were obtained by averaging appropriately between fifth-neighbor models of Ni and Pd.

Force constant	Pd	Ni	$Ni_{55}Pd_{45}$
$1xx$	19159 ± 236	17319	18221
$1zz$	−2781 ± 414	−436	−1396
$1xy$	22405 ± 440	19100	21085
$2xx$	1514 ± 348	1044	1362
$2yy$	147 ± 224	−780	−459
$3xx$	712 ± 257	842	821
$3yy$	331 ± 136	263	212
$3yz$	288 ± 207	−109	272
$3xz$	489 ± 101	424	606
$4xx$	−1115 ± 118	402	−221
$4zz$	−117 ± 175	−185	10
$4xy$	−849 ± 393	660	−561
$5xx$	178 ± 240	−85	21
$5yy$	−205 ± 110	7	−55
$5zz$	−254 ± 145	18	−65
$5xy$	144 ± 130	−35	28
$6xx$	84 ± 91		
$6yz$	−202 ± 176		
$7xx$	−28 ± 128		
$7xy$	96 ± 134		
$7zz$	−7 ± 51		
$7yz$	10 ± 19		
$7xz$	14 ± 28		
$7xy$	29 ± 52		
$8xx$	97 ± 146		
$8yy$	−49 ± 129		

Au).

Ni and Pd form solid solutions at all concentrations, and no indications of long-range order have been observed down to 0 °C. At 45-at.% Pd, the phase diagram[18] shows that the liquidus and solidus touch. At this concentration, very convenient for a study of a high-concentration mass-disordered crystal, it was thought that a homogeneous single crystal should be relatively easy to grow. The absence of any observed ordering transformations in the Ni-Pd system is one of its most attractive features, and leads one to hope that the condition of complete random substitutional disorder is satisfied as well as is possible for a real system in which there is a large mass difference between the components. Most other solid solutions that show a minimum melting temperature (liquidus and solidus must touch at the corresponding concentration) are more complicated than Ni-Pd in other respects. For example, at temperatures below about 400 °C, Cu-Au alloys tend to form the ordered structures Cu_3Au and CuAu for compositions near 25 and 50-at.% Au. The minimum melting temperature for Cu-Au solid solutions occurs at 56.5-at.% Au. Specimens of an ordered alloy can often be easily disordered by quenching, but the tendency to form an ordered structure at all leads one to expect that short-range order will still be present.

Like other fcc transition and noble metals, the dispersion curves[19,20] of Ni and Pd are dominated by large, almost central, nearest-neighbor forces. Palladium has been particularly thoroughly studied,[20] partially in order to investigate a fairly strong temperature-dependent anomaly in the $[\zeta\zeta 0]T_1$ branch, now believed to be caused by the Kohn effect.[21] The anomaly is only strong in this particular branch; the dispersion curves of Pd are otherwise very simple. Ni has no unusual features in its dispersion curves. The force constants derived from the dispersion-curve measurements are about 15% larger in Pd than in Ni, as shown in Table II. The elastic constants of Pd and Ni are comparable in size, but show significant differences (Table I). The lattice-dynamical properties of Ni and Pd bear somewhat the same relation to one another as do those of Cu and Au (aside from the different mass ratio involved).

The neutron scattering properties of Ni and Pd are reasonably favorable. The fairly high incoherent cross section of nickel was at first thought to be a potentially serious disadvantage, but in practice, this did not turn out to be much of a problem. The scattered neutron distributions are always dominated by the coherent scattering, even for high-frequency modes with large widths. The substantial difference between the coherent scattering lengths of Ni and Pd produces additional incoherent scattering (about 0.5 b per atom in $Ni_{55}Pd_{45}$), but this is much smaller than the incoherence produced by the Ni itself (about 2.7 b per atom in the alloy). However, the different coherent scattering lengths must be properly accounted for when experimental coherent inelastic cross sections are compared with theoretical calculations.

B. Specimen crystal

Our specimen of $Ni_{55}Pd_{45}$ was grown by the Czochralski method by Research Crystals Inc. of Richmond, Va. The crystal as grown was about 1.6 cm in diameter by 10 cm in length, and had a [100] axis about 20° off the cylinder axis. The top 2 cm of the boule is a fairly good crystal, with a mosaic spread of about 0.5° full width at half-maximum (FWHM), but the mosaic progressively increases further down the crystal to about 3° FWHM at the bottom end of the crystal. The mosaic distribution is anisotropic, and it was found that if the

crystal was mounted with the cylinder axis approximately horizontal, all the observable rocking curves were in the range 0.8° to 1.2° FWHM. Since the collimation in a crystal spectrometer is typically 2° or 3° FWHM vertically and 1° horizontally, it was felt that the effects of the mosaic of this crystal should not be too serious, although not negligible. Some of the observations were made on the uncut boule, with the cylinder axis horizontal. However, with this specimen some modes had to be observed in a consistently bad geometry. Accordingly, a specimen consisting of two sections, 2.5 cm in length, cut from the more perfect end of the boule and mounted one above the other, was used for the rest of the measurements. Checks were made that the neutron groups measured with the two specimens were in agreement.

The crystal was characterized with respect to its lattice constant (found to be 3.720 ± 0.002 Å) and its homogeneity by neutron diffraction, following the method of Ng *et al.*[22] The method yields peaks similar to power diffraction peaks. The position of the peak gives the lattice constant of the alloy single crystal. The width of the peak above the resolution width gives the spread in lattice constant. If the lattice constant depends reasonably strongly on composition, the position and width of the peak thereby give, respectively, the mean composition and inhomogeneity (spread in composition) of the alloy. The width of the characterization peak was not significantly larger than the experimental resolution width. This fact indicates very good homogeneity (in a macroscopic sense), as might have been expected from the phase diagram. The composition, as determined by a density measurement, was found to be $c_{Pd} = 45.16 \pm 0.10$ at.%, in very good agreement with the nominal composition and with the measured lattice constant.[14]

C. Neutron scattering measurements

All of the measurements were taken on the McMaster University triple-axis spectrometer[23] at the NRU reactor, Chalk River. The constant-Q mode was used throughout, with the specimen at room temperature.

For some of the less-intense scattered-neutron distributions corresponding to longitudinal modes of higher frequency, a double-peak structure was observed, with one peak close to the expected frequency of the longitudinal mode, and a lower-frequency peak near the frequency of a transverse mode of the same wave vector. Because the standard one-phonon cross-section formula contains a factor $(\vec{Q} \cdot \vec{\xi})^2$, where $\vec{Q}$ is the wave-vector transfer to the crystal in the scattering, and $\vec{\xi}$ is the phonon polarization vector, the "transverse" peak should be absent in a crystal with no disorder if one chooses $\vec{Q}$ parallel to the phonon wave vector $\vec{q}$. It is possible that such a peak could arise from a real dynamical effect caused by the disorder (effectively an uncertainty in the polarization vector). However, this feature has been investigated quite thoroughly because of its possible dynamical origin and has been demonstrated conclusively to be spurious. It is almost certainly caused by multiple scattering,[24] i.e., Bragg reflection of the incident (scattered) beam prior (subsequent) to scattering from a phonon. The effect can be eliminated or almost eliminated by properly choosing the instrumental variables for the constant-Q scans.

D. Treatment of resolution

In order to extract the natural widths which are the primary results of this experiment, it was necessary to be able to determine reliably the experimental resolution widths. This was done mainly by means of resolution calculations based on the formulation of Cooper and Nathans.[25] Several different computer programs were used to do this, two of which were written at McMaster University by A. Larose and J. R. D. Copley, and two others which originated from Brookhaven National Laboratory (BNL). Larose's program and one of the BNL programs assume a planar approximation for the dispersion of the frequencies inside the resolution ellipsoid. Almost all of the calculations were made with the planar approximation. The resolution calculations were checked in selected cases by measuring, under experimental conditions very nearly the same as in the primary experiment, the widths of neutron groups in pure copper, which has dispersion curves very similar to those of $Ni_{55}Pd_{45}$. The calculated widths and copper widths were found to be in agreement for all cases tested, within the errors of about 15 or 20%.

Special attention was given to the possibility of an extra contribution to the resolution width from the vertical mosaic of the crystal and also, for the $[\xi\xi\xi]$T branch, from the nonplanar nature of the dispersion surface[26] in the neighborhood of that branch. Both of these turned out to be fairly small effects. The corrections that were indicated were typically a few percent of the planar-approximation resolution widths (the latter were in the range of 0.2–0.7 THz).

The resolution widths were extracted from the experimentally observed widths by assuming that the observed line shape could be adequately approximated by the convolution of a Gaussian resolution function with a Lorentzian natural line shape. This assumption was tested by using the quasi-Lorentzian line shapes produced by low-concentration mass-defect theory for 45-at.% Pd in Ni, and was found to be generally well justified.

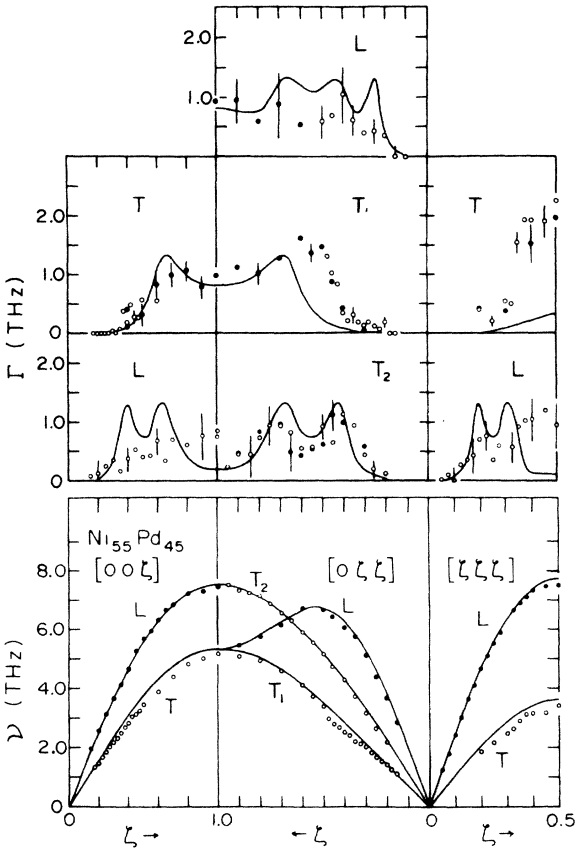

FIG. 1. Dispersion curves (bottom) and disorder-induced widths (top) observed along three symmetry directions in $Ni_{55}Pd_{45}$. In the top figure, for a given branch, the open circles represent measurements with better resolution than the filled circles. The wave-vector coordinates are in units of $2\pi/a$. The solid lines represent (top) widths predicted by the self-consistent theory of Taylor, and (bottom) a Born–von Kármán model of a mean crystal with force constants and mass averaged between Ni and Pd (55 to 45%).

III. RESULTS AND DISCUSSION

A. General description of experimental results

The neutron scattering measurements on $Ni_{55}Pd_{45}$ are summarized in Fig. 1, which shows the disorder-induced widths (top) and the mean frequencies (bottom) of the modes, plotted against reduced wave vector. The widths (see Sec II) are the natural widths obtained after extracting the resolution from the experimental widths. Seven branches have been measured along the symmetry directions [001], [110], and [111].

In each branch, the modes show significant natural widths at larger wave vectors. In the low-frequency regions, the widths are small but start to become significant when the phonon frequency reaches about 3 THz. In the transverse branches, the widths show behavior characteristic of resonance modes, with the resonance frequency varying from about 3 THz to slightly more than 4 THz. The resonance is strongest and of lowest frequency (about 3 THz) in the $[\zeta\zeta\zeta]$T branch, strong in the $[0\zeta\zeta]T_1$ branch (also at about 3 THz), and weaker, but still evident, in the $[0\zeta\zeta]T_2$ and $[00\zeta]$T branches at a higher frequency (slightly more than 4 THz). In the $[0\zeta\zeta]T_2$ branch, there is also a strong indication of a second resonance of higher frequency (around 7 THz).

Note that in the $[\zeta\zeta\zeta]$T branch, the width (FWHM) of the zone-boundary phonon is about 0.7 of its mean frequency. The dramatic increase in width for phonons in this branch is shown in Fig. 2. The mean frequencies and widths for the wider groups in this branch were corrected for the distortion caused by the temperature-dependent factor $[n(\nu)+1]$ in the cross section, where $n(\nu)$ is the Bose-Einstein population factor. In order to check that anharmonicity does not significantly affect the width, the $[\zeta\zeta\zeta]$T zone-boundary mode was also measured at a lower temperature (about 150 °K). The width was little affected by the change in temperature. Figure 3 shows more neutron groups typical of those used in obtaining the data points of Fig. 1. For each of the three branches $[0\zeta\zeta]T_1$, $[0\zeta\zeta]$L, and $[\zeta\zeta\zeta]$L, a pair of groups is shown, one group of low wave vector and the other of higher wave vector. For the latter, broadening is apparent in each of the three branches, but is

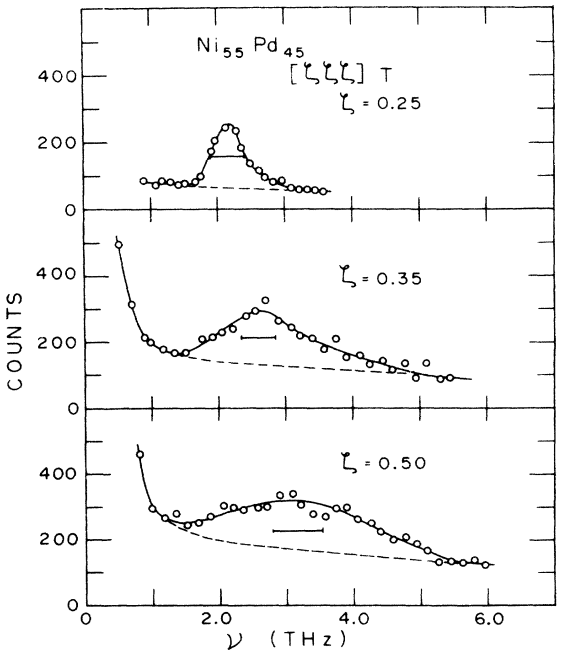

FIG. 2. Observed neutron groups for the $[\zeta\zeta\zeta]$ T branch of $Ni_{55}Pd_{45}$. The horizontal bars represent the calculated resolution widths (FWHM).

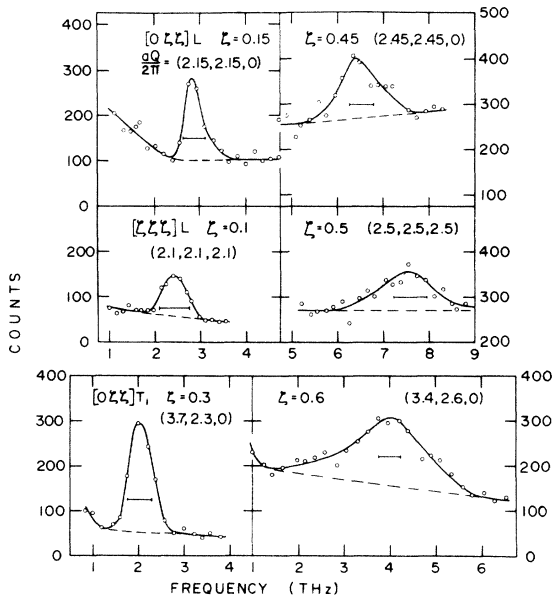

FIG. 3. Typical neutron groups used in obtaining the data points of Figs. 1 and 4, showing modes of low and higher wave vector in three different branches. In each case, the horizontal bar represents the calculated resolution width (FWHM).

especially pronounced in $[0\zeta\zeta]T_1$.

There appears to be a qualitative difference between transverse and longitudinal modes with respect to the behavior of the natural widths. The longitudinal widths are generally smaller and show little sign of the existence of resonant perturbation. There is some indication of the presence of two resonances in the $[\zeta\zeta\zeta]L$ branch (at about 4.5 and 7.5 THz) but within errors, the width could just increase monotonically from the origin to the zone boundary. In the $[00\zeta]L$ branch, there is no indication at all of resonances and the amplitude of the width is smaller than for the other branches.

Turning now to the dispersion curves themselves, we find the behavior of the natural widths complemented in the behavior of the frequencies. The solid lines of Fig. 1 (bottom) represent a fifth-neighbor Born–von Kármán model of a mean crystal with force constants and mass averaged between those of Ni and Pd (55 to 45%). The model was in no way fitted to the measurements. The force constants are listed in Table II. As one can see, there is very good over-all agreement of the measured frequencies with this model. In fact, the regions in which there are significant deviations from the model are generally regions where a resonance occurs and the natural widths are large. This is especially apparent in the $[0\zeta\zeta]T_1$ branch, where a prominent kink in the dispersion curve occurs at $\zeta = 0.5$. The frequencies in the $[\zeta\zeta\zeta]T$ and $[00\zeta]T$ branches are also low at higher wave vectors, where large natural widths occur. There are also less certain regions of lowered frequency in the low-wave-vector part of the $[0\zeta\zeta]T_2$ branch and near the zone boundary in the $[\zeta\zeta\zeta]L$ branch, both of which are also regions in which the natural widths are fairly large. In the $[00\zeta]L$ branch, where no resonances are apparent and the widths are small, the mean-crystal model gives almost exact agreement with the measured frequencies. The behavior of the frequencies thus seems to indicate that force-constant changes from the pure substances to the mixed crystal must be quite small in an average sense, although there may be fairly large fluctuations of the force constants between individual atoms about the average values.

B. Important features of the experimental results

1. Widths

Perhaps the most significant information contained in the measurements lies in the order of magnitude of the widths for the alloy. The measurements have shown that, in the presence of the substantial amount of mass disorder implied by a heavy-atom concentration of 45 at.% and a mass ratio of 1.8, phonons can still be considered to exist, though often with large widths, ranging up to 70% of the mode frequency. The order of magnitude of the widths and their qualitative behavior can be understood on the basis of fairly simple models, but quantitative understanding is much more difficult.

When the natural widths are plotted as functions of frequency or wave vector for each branch, the data for each transverse branch indicate the presence of a peak in the width at a phonon frequency of around 3 to 4 THz. It is thus apparent that behavior characteristic of resonance modes persists into the high-concentration regime. Calculations based on mass-defect theory[27] for isolated defects or small finite concentrations show that well-defined resonances can occur in a monatomic alloy for a mass ratio of 2 to 1. That a Pd atom has resonance modes in a Ni host in thus to be expected, but it is rather surprising that such clearly defined resonances exist at a concentration of 45-at.% Pd.

Now turning to consider the details of the experimental results, the most striking feature of the behavior of the natural widths shown in Fig. 1 is the pronounced branch dependence, qualitatively very similar to that seen in Cu(Au). The dependence can be seen more clearly in Fig. 4, where the results have been plotted against the unperturbed frequency for each branch. The unperturbed frequency is the frequency of the corre-

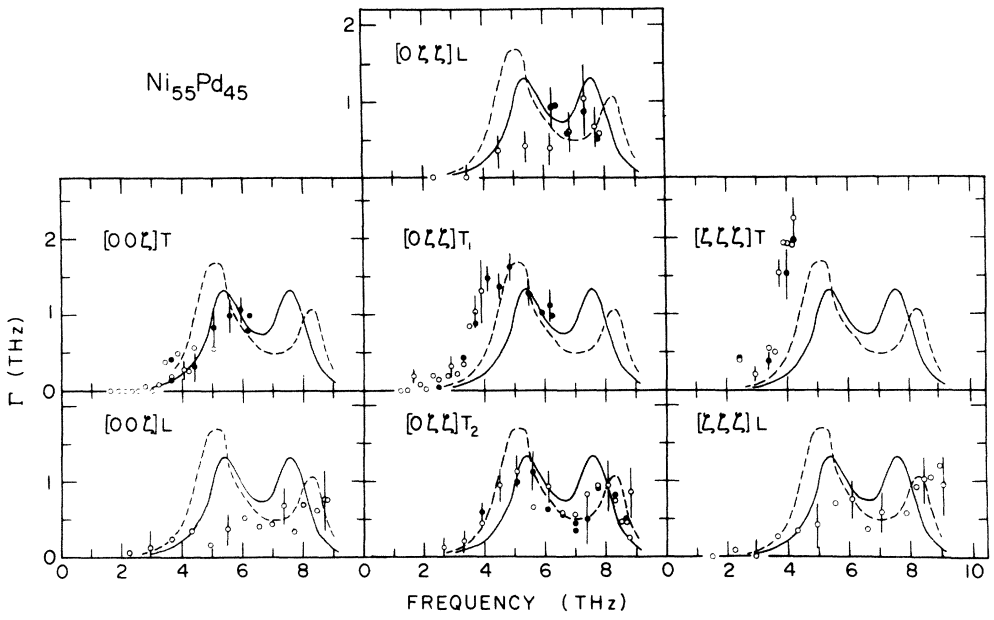

FIG. 4. Natural widths for $Ni_{55}Pd_{45}$ plotted against reference-lattice (Ni) frequency for each branch. The solid lines represent the predictions of the self-consistent theory, and the dashed lines represent those of low-concentration theory.

sponding mode (same reduced wave vector) in a lattice with Ni mass and force constants averaged between Ni and Pd. Figure 4 should be compared in detail with Fig. 5, which shows similar data for Cu(9-at.% Au), and which has been laid out in a similar manner to permit a direct and easy comparison.

Figure 5 includes results for the [ζζζ]T branch in Cu(9-at.% Au) which have not previously been reported. It should be noted that the solid and dotted lines in Fig. 5 have a meaning different from the lines in Fig. 4. In Fig. 5, the lines were obtained from low-concentration mass-defect theory, the solid lines directly from the imaginary part of the phonon self-energy, and the dotted lines from the widths (FWHM) of the calculated neutron scattering cross sections. If the calculated widths were small compared with the frequencies of the phonons, the line shapes of the excitations would be almost Lorentzian, and the solid and dotted lines would agree closely. The difference between the solid and dotted lines reflects the non-Lorentzian character of the calculated line shapes, some of which were asymmetric or showed double peaks. Details of the calculations and a figure showing some of the calculated line shapes are given by Svensson and Kamitakahara in Ref. 1.

For the four branches which have been studied in both systems, the over-all pattern of the resonances in the widths is remarkably similar. The amplitude of the width is largest in the [ζζζ]T branch, next largest in the [ζζ0]T_1 branch, smaller in the [00ζ]T branch, and very small in [00ζ]L. In fact, it was only after the Ni-Pd experiment had been almost completed, and the similarity of the pattern of the resonances had been noted, that the [ζζζ]T branch was measured in Cu(3-at.% Au) and Cu(9-at.% Au). As anticipated, the resonances were found to be strong and sharp.

Despite the pronounced similarities, the behavior of the widths is not identical for the Cu(Au) and Ni-Pd systems. The following differences should be noted:

(i) The resonances occur at higher values of the reduced wave vector in Ni-Pd than in Cu(Au), i.e., at higher frequencies.

(ii) In [ζζ0]T_1, which is the only branch where we can compare the width of the resonance for the two systems, the resonance is broader in Ni-Pd than in Cu(9-at.% Au).

(iii) The amplitude of the width in Cu(Au), per heavy atom, is about twice as large as in Ni-Pd.

Each of these tendencies, (i), (ii), and (iii), would perhaps be expected because of the differences in the mass ratios for the two systems, although concentration-dependent effects may also be present.

(iv) The rise in the width on the low-frequency side of the resonance occurs at about the same unperturbed frequency (approximately 2.6 THz) in the three branches [ζζζ]T, [ζζ0]T_1, and [00ζ]T in Cu(9-at.% Au). For Ni-Pd, the rise in the [00ζ]T branch occurs at about 5 THz, a frequency substantially higher than in [ζζ0]T_1 or [ζζζ]T; in both

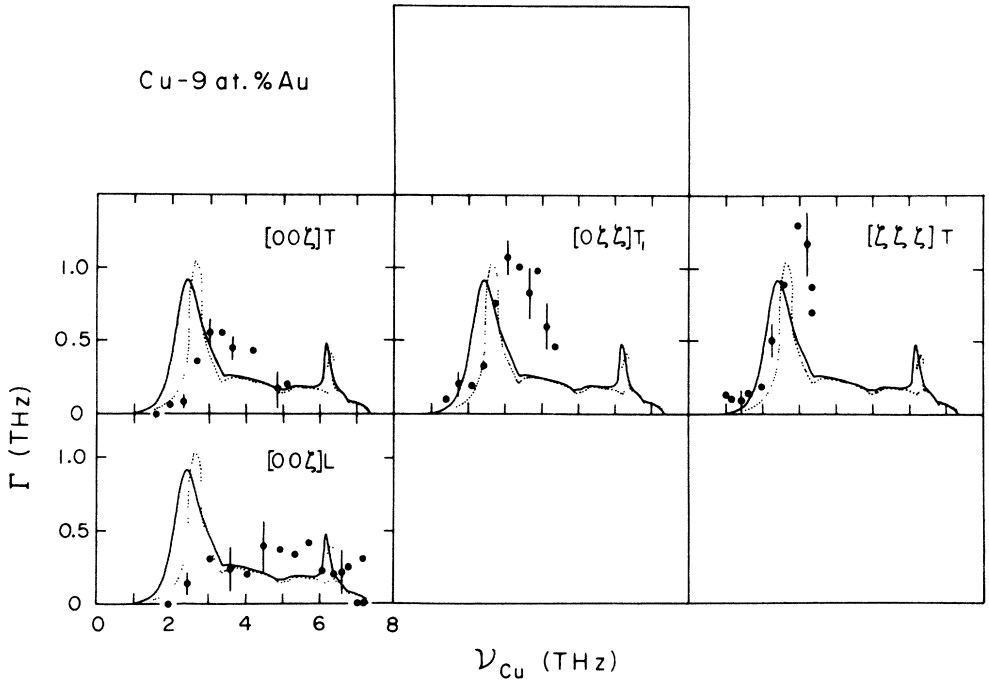

FIG. 5. Natural widths for Cu(9-at.% Au) plotted for each branch against the frequency of the corresponding mode in pure copper. The lines represent the widths as calculated from low-concentration mass-defect theory, and do not have the same meaning as the lines in Fig. 4. Refer to the text for more explanation of the calculated lines.

of the latter two branches, it occurs at about 3.7 THz.

In the previously reported work[1] on Cu(Au), the conclusion was drawn that force-constant changes provided the only logical explanation for the pronounced and similar branch dependences of the widths in Cu-3-at.% Au and in Cu-9-at.% Au. By extension, force-constant changes must also be important for $Ni_{55}Pd_{45}$, unless there is an unexpected similarity between the effects produced by large concentrations and force-constant changes. The changes must have a physical origin that is common to the Cu(Au) and Ni-Pd systems. The most obvious consideration is the increased overlap of the heavy atoms with their nearest neighbors, because of their larger size. The lattice constants of Pd and Au are about 11 and 10% larger, respectively, than those of Ni and Cu.

2. *Frequencies*

It is relatively more difficult to extract meaningful information about disorder effects from the phonon frequencies than from the widths, although there must be frequency shifts associated with the disorder. As one can see from Fig. 1 (bottom), the mean-crystal model reasonably describes the general behavior. The regions of lowered frequency, near $\zeta = 0.45$ in $[\zeta\zeta 0]T_1$, at higher wave vectors in the $[\zeta\zeta\zeta]$T and $[00\zeta]$T branches, and less certainly, in the low-wave-vector part of the $[\zeta\zeta 0]T_2$ branch and near the zone boundary in the $[\zeta\zeta\zeta]$L branch, indicate a complementarity to regions of large widths. However, it is not correct to regard the difference between the mean-crystal model and the measured frequencies as necessarily disorder-induced frequency shifts, since there is no reason to believe that the force constants obtained by averaging between Ni and Pd give exactly the average force constants in the alloy. The difference between the model force constants and the real force constants will give rise to a small but unknown shift in the phonon frequencies. The disorder-induced shift, which is superimposed on this "average" shift, will also be relatively small for the Ni-Pd alloy, and is therefore very difficult to separate out. The anomaly[20] which occurs in the $[\zeta\zeta\zeta]T_1$ branch of pure Pd is another source of uncertainty in how to extract disorder-induced frequency shifts, although the nature of the anomaly is now believed[21] to be a Kohn effect of a sort that would not be present in an alloy of $Ni_{55}Pd_{45}$.

C. Comparison with theory

1. *Perturbation theory*

If one uses perturbation theory to second order in the mass differences, an approximation is obtained which is essentially restricted to isotopic

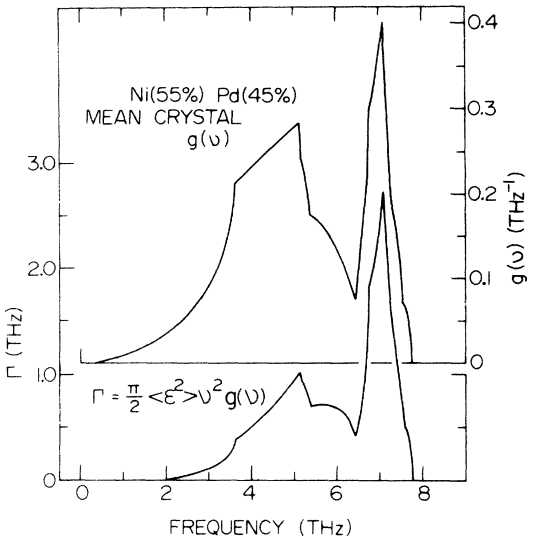

FIG. 6. Widths Γ for $Ni_{55}Pd_{45}$ predicted by perturbation theory. The top portion of figure shows the reference-lattice frequency distribution $g(\nu)$ used in the calculation.

disorder. The approximation is therefore not really applicable to the present experimental situation. However, it is by far the simplest calculation among those to be discussed here, and does in fact give a reasonable first estimate for the disorder-induced widths, providing a basis for comparing more complicated theories.

The perturbation theory can be done by working directly in terms of the normal modes[8] of the system, or by using Green's functions.[12] The first approach is based on work by Mattis.[28] The latter approach gives a slightly more general result, and is also of some value in assessing the nature of the approximation. The theory predicts that a phonon (with frequency ν) in the mean (virtual) crystal should have a width (FWHM) in the alloy given by $\frac{1}{2}\pi\langle\epsilon^2\rangle\nu^2 g(\nu)$, where $g(\nu)$ is the phonon frequency distribution in the mean crystal (normalized to unity) and ϵ is the mass-defect parameter relative to the mean crystal; i.e., $\epsilon = [1 - M_l/\langle M\rangle]$. The averages indicated by the brackets are over all lattice sites l.

The widths predicted for $Ni_{55}Pd_{45}$ are shown in Fig. 6, together with the frequency distribution $g(\nu)$ used in the calculation. When compared with the experimental widths of Fig. 4, these widths are seen to be clearly of the right order of magnitude. The frequency at which the widths should start to become large is predicted to be about 3.5 THz, which is approximately correct. Also, two "resonances" are predicted, corresponding to the two major peaks in $g(\nu)$, in agreement with observations on the $[\xi\xi 0]T_2$ branch and, perhaps, the $[\xi\xi\xi]$L branch. However, the first (lower-frequency) resonance appears to be too small, typically by about 40 to 50%, while the second resonance is too large by about a factor of 3. It is very likely that the latter fact arises from the lack of self-consistency in the perturbation theory. The proportionality of the width to $g(\nu)$ reflects the ability of a phonon to decay into other phonons close to it in frequency. The large amplitude predicted by the perturbation theory for the second resonance is produced by the large number of modes with frequencies near 7 THz in the reference lattice. However, it seems reasonable that the reference lattice $g(\nu)$ does not really represent the density of phonon states available for decay, but that since the phonons have become smeared out in frequency, the amplitude of the second peak in $g(\nu)$ has been greatly reduced. It might be better to use $g(\nu)$ for the imperfect crystal since, for high-concentration isotopic disorder, the imperfect crystal is almost certainly a better approximation for the environment of any given atom.

2. *Self-consistent theory (CPA)*

The coherent-potential approximation (CPA) is now a well-known theory for the electronic structure of disordered alloys. The analogous theory for phonons was formulated several years ago by Taylor.[29]

The theory assumes a monatomic structure (although it can be generalized to the diatomic case) with no long-range or short-range order, and no force-constant changes. It neglects fluctuations in the configuration of other atoms around an individual atom, and the scattering of phonons by impurity pairs and impurity complexes. "Host"- and "impurity"-type atoms are treated on an equivalent basis, an essential property for a high-concentration theory. In the limit of very small concentrations, the low-concentration theory is correctly obtained, but the initial effects that occur as c is increased, such as the broadening of a local mode, are not properly described.

The main success of this theory is the agreement obtained with the numerically derived frequency distributions of Payton and Visscher.[30] In one and three dimensions, and for fairly large mass ratios (up to 3), the agreement is good, except that some detailed structure in the computer-derived distributions, thought to arise from impurity pairs and complexes, is not reproduced. In this respect, the agreement for three dimensions is better than for one dimension. Both these characteristics are to be expected from the nature of the approximation.

In spite of the agreement with the numerical work (which one should regard as computer exper-

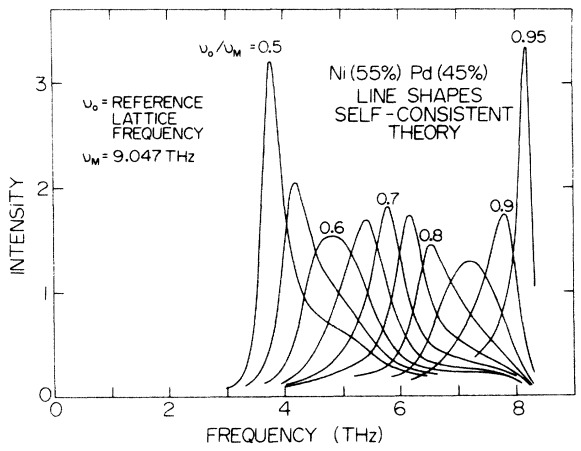

FIG. 7. Line shapes of the coherent neutron scattering cross section for $Ni_{55}Pd_{45}$ predicted by the self-consistent mass-defect theory of Taylor. The difference between the scattering lengths of Ni and Pd has been taken into account. ν_M is the maximum reference-lattice (Ni) frequency.

iments), it should be pointed out that a quantity such as a frequency distribution is a relatively insensitive criterion by which to judge a theory that attempts to give a detailed description of the imperfect-crystal dynamics. Especially for modes within the band, much of the detailed behavior of the modes has been averaged out; in particular, one has lost information about the widths of the phonons within the band, or even whether phonons remain a good description. Comparisons of calculations with observations on the behavior of individual phonons, such as can be seen by neutron scattering, or perhaps by more complicated types of computer experiments, represent more stringent tests of theory.

In the present experiment on $Ni_{55}Pd_{45}$, the concentration and mass ratio are in the regime where CPA might be expected to work in a nontrivial way. The major obstacle to a critical comparison of experiment with theory is the probable importance of force-constant changes in this alloy. However, CPA is clearly in better agreement with experiment than the perturbation theory described above.

The solid lines in Fig. 4 represent the widths calculated for $Ni_{55}Pd_{45}$ from the self-consistent theory, plotted as functions of the reference-lattice frequency. Each of the solid lines is the same, since this approximation produces widths that depend only on the reference-lattice frequency, and not on the branch. The calculated widths are also shown as solid lines in Fig. 1 (top), where the results are plotted against wave vector. The plot against frequency, Fig. 4, permits an easier comparison of the theoretical widths with experiment. However, the plot against wave vector shows the behavior of the phonon frequencies at the same time, and summarizes almost all the results of the experiment. The difference between the scattering lengths of Ni and Pd has been taken into account in the calculations.

Comparing the experimental widths with the theory, we find substantial qualitative similarity, but not quantitative agreement. The presence of resonances is correctly predicted, but the branch dependence of their strengths and frequencies is not. In the $[0\zeta\zeta]T_2$ branch, both of the predicted resonances are observed. The qualitative agreement is poorest for the longitudinal branches (especially $[00\zeta]L$), where we observe no well-defined resonances.

We have carried out calculations of the neutron scattering cross sections for three theories. These are the CPA, the average-t-matrix approximation (ATA), and low-concentration mass-defect theory. The latter two theories are discussed below. All three theories predict line shapes with pronounced asymmetries for phonons with frequencies in the regions of the resonances. The CPA line shapes are shown in Fig. 7 for several values of the reference-lattice frequency ν_0. The asymmetries can be described as a tendency for more scattering to occur near the resonance frequencies, about 4.8 and 7.2 THz on the abscissa scale of Fig. 7. That is to say, the line shape of a mode with a frequency slightly lower or higher than that of a resonance tends to have a "shoulder" or a pronounced tail over the resonance region. If a line shape peaks right on a resonance, the line shape is symmetric but broad.

Most of the line shapes observed in the experiment were nearly symmetric. For some neutron groups corresponding to transverse phonons with frequencies just below the first resonance, definite asymmetries to the right were observed. Such asymmetries were evident in the groups for $[\zeta\zeta\zeta]T$, $\zeta = 0.35$ in Fig. 2, and for $[\zeta\zeta 0]T_1$, $\zeta = 0.4$ and 0.45 in Fig. 8. In most cases, the energy resolution, typically 0.5 THz FWHM, and counting statistics were probably not adequate to detect the other types of asymmetries, even if present.

3. *Defects from the mean lattice (ATA)*

An approximation that is somewhat less realistic than CPA, but possibly still reasonable, is to consider the virtual crystal (with the mean mass at each site) as the reference lattice and then to calculate the scattering from a concentration c of heavy "defects" and a concentration $(1-c)$ of light defects, using the methods of the low-concentration theory of Elliott and Taylor.[31] Leath and Goodman[32] have calculated frequency distributions based on this approximation (the average-t-matrix

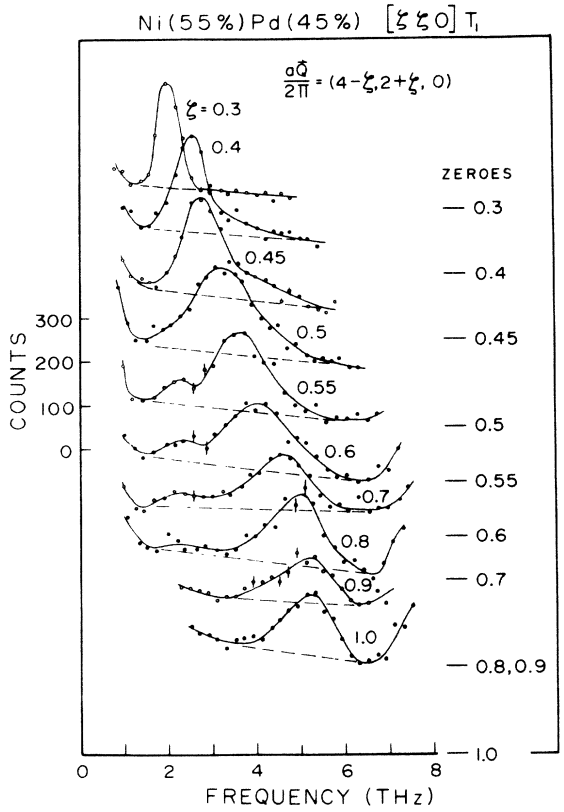

FIG. 8. Neutron groups for the $[\zeta\zeta 0]$ T_1 branch in $Ni_{55}Pd_{45}$. The structure at around 2.5 THz for $\zeta = 0.55$, 0.6, and 0.7 is not necessarily real, but is an interesting indication, and is similar to structure predicted by low-concentration mass-defect theory. The rise in intensity at about 7.5 THz for $\zeta = 0.6$ to $\zeta = 1.0$ is caused by a contaminant energy in the incident neutron beam.

approximation, or ATA), and compared their results with the computer experiments of Payton and Visscher,[30] as was done for CPA by Taylor.[29] The agreement with the computer experiments is somewhat poorer for ATA than for CPA, especially near the band edges, but still appears to provide a sensible description at all concentrations.

However, we found that calculations of the phonon self-energy and line shapes in neutron scattering reveal two rather surprising facts, which indicate that the approximation is not as good as might be inferred from the frequency distributions. First, the self-energy turns out to be very close to that calculated from the perturbation theory discussed above. The inadequacies pointed out for the latter must therefore also apply for ATA. Second, unrealistic double-peaked line shapes, definitely in disagreement with experiment, are predicted by ATA in the frequency region around 7 THz, where, as discussed above for the perturbation theory, the self-energy is not expected to be accurate.

4. Low-concentration theory

Calculations based on low-concentration mass-defect theory[31] for 45-at.% Pd defects in a Ni host have also been carried out. The widths derived from the calculated line shapes are shown in Fig. 4 as dashed lines. In the low-concentration theory, the immediate environment of an impurity atom is taken to be the host lattice, but multiple scattering of lattice waves from the distribution of individual impurities is considered. The low-concentration theory should in principle not be applicable to $Ni_{55}Pd_{45}$, but in fact the over-all agreement with the experimental widths is about as good (or bad) as for the self-consistent theory.

The line shapes calculated for the low-concentration theory (not shown here) are in generally poorer agreement with experiment than those for CPA, but better than those for ATA. The low-c theory predicts double peaks and "shoulders" for neutron groups with mean frequencies around 4 or 5 THz. Some qualitatively similar features may have been observed in the $[\zeta\zeta 0]T_1$ branch ($\zeta = 0.55$, 0.6, and 0.7 in Fig. 8), but this is not certain because of counting statistics and the always present possibility of a spurious effect of trivial experimental origin.

The low-concentration theory lacks the necessary host-defect symmetry on a *bona fide* high-concentration theory. Applying the theory with a concentration of 55-at.% Ni defects in Pd would certainly not give sensible results. In this respect, its application to the present experimental situation is much less appealing than the application of the self-consistent theory.

D. Other factors

The branch dependence of the natural widths could arise from factors other than force-constant changes.

1. Short-range or long-range order

Structural order in the alloy could be influencing the crystal dynamics, although the phase diagram[18] shows no indication of ordered phases in the Ni-Pd system down to 0 °C. We have partially investigated this possibility by neutron diffraction by measuring the intensity at all reciprocal lattice points with indices (h, h, k), $h, k \leq 4$, using a Ge(111) analyzer to eliminate second-order effects. Within the limited accuracy of the experiment, there is no long-range order. (The upper limit on the intensity of superlattice peaks is less than $\frac{1}{2000}$ of that of a fcc peak.) Short-range order is still possible; to what extent its presence would influence the widths in Ni-Pd is difficult to guess. The effect of long-range order would[9] be to produce apparently large widths in regions where the degen-

eracy of two branches is lifted by the lowering of the crystal symmetry. The effect of short-range order would be qualitatively similar, but probably less pronounced. Some theoretical work that does indicate that the effect of short-range order is probably small has been carried out by Hartmann[33] for the case of Cu(9-at.% Au).

2. *Scattering from impurity pairs and impurity complexes*

The approximation that has been made in the theories discussed above is to consider only scattering of the lattice waves from single sites, and to treat the total scattering from a single site as the sum of all the multiply scattered waves. The scattering from an atom is assumed not to depend on its environment. This is a reasonable approximation for very low impurity concentrations, where the probability of adjacent impurities is small, and the environment of most defect atoms looks like a lattice with all host atoms. However, it is a questionable assumption for higher impurity concentrations, and perhaps an unreasonable one for a mixed alloy such as $Ni_{55}Pd_{45}$. The self-consistent theory says that a single-site approximation may still be usable for very high concentrations in three dimensions because, in Taylor's words, although the environmental fluctuations are "large in number, they are mainly weak in strength." A number of attempts have been made to extend the theory to include pair and cluster scattering (the earliest by Aiyer *et al.*[34]), but to our knowledge, successful calculations in three dimensions based on these extended theories have not yet been carried out, apparently because of analytic difficulties.[35]

One might expect that the effect of pair and higher-order scattering would be to broaden and to increase the frequency of the resonances. The shift and width would become dependent on branch, even with no force-constant changes. In $Ni_{55}Pd_{45}$, it is fairly certain that the pattern of the branch dependence in the widths comes largely from force-constant changes so that it is not possible to isolate any effects of pair and higher-order scattering.

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