

IN-BAND MODES OF VIBRATION OF A COPPER-3 AT.% GOLD ALLOY*

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The atomic vibrations in a single crystal of Cu-3 at.% Au have been studied using inelastic neutron scattering. The line shapes and widths of the neutron groups, and the shifts from the corresponding frequencies for the host (pure copper), agree substantially with calculations based on the theory of Elliott and Maradudin, but appear to show slight deviations which are in the same direction as, but much less marked than, those exhibited by the results of previous measurements on single crystals of Cu-9.3 at.% Au.

The detailed effect of heavy-mass impurities on the lattice vibrations of a host was first studied experimentally for a single crystal of Cu-9.3 at.% Au by means of inelastic neutron scattering.¹ The results were not in good agreement with calculations based on the theory derived by Elliott and Maradudin² for small concentrations of randomly placed, substitutional, heavy-mass impurities. Similar measurements³ on a single crystal of Cr-3 at.% W also gave results which were in disagreement with this theory, though not in the same way.

In an attempt to get better agreement with the theory, and to determine its limitations, new measurements have been carried out on a single crystal of Cu-3 at.% Au. The crystal was obtained from Research Crystals, Incorporated, Richmond, Virginia. Its lattice constant was taken⁴ to be 3.631 Å (fcc) at room temperature. (A recent neutron-diffraction measurement⁵ has given the value 3.633 ± 0.001 Å at 22°C, with a total spread in lattice constant of about ± 0.009 Å, thus verifying the composition, but indicating some inhomogeneity as might be expected from the phase diagram.⁶) The measurements were carried out at room temperature using the McMaster University triple-axis spectrometer⁷ in the constant- \vec{Q} mode of operation with fixed incident-neutron energy ($E_0 = 23.60$ meV) and variable outgoing-neutron energy ($E' \geq 9.33$ meV); (200) planes of copper crystals were used for the analyzer and monochromator. The $[0\zeta\zeta] T_1$ branch (polarization vector parallel to $[0\bar{\zeta}\zeta]$) was selected for initial study. Results⁸ for the $[0\zeta\zeta] T_1$ branch in pure copper were taken with the same spectrometer under identical conditions.

According to the theory of Elliott and Maradudin² (see also Ref. 1), the line shapes for

an alloy crystal are given by the expression

$$L(\nu, \nu_0) = \frac{c V_2(\nu)}{[\nu^2 - \nu_0^2 - c V_1(\nu)]^2 + [c V_2(\nu)]^2}, \quad (1)$$

where c is the (small) impurity concentration, and ν_0 is the frequency of the corresponding normal mode of the pure host crystal. The func-

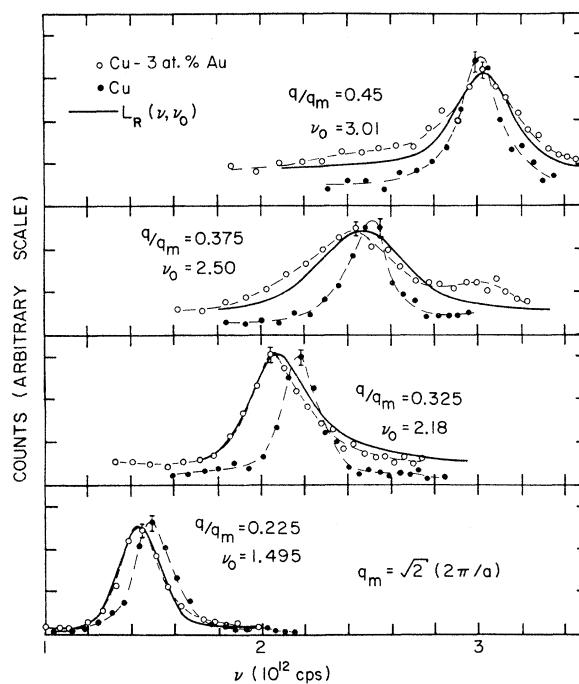


FIG. 1. Corresponding pairs of neutron groups and the calculated resolution-broadened line shapes, $L_R(\nu, \nu_0)$, for the alloy (see text). The groups are labeled with the value of the reduced wave vector, q/q_m , and the frequency, ν_0 , assigned to the copper group. The bump at the high-frequency end of the alloy group for $q/q_m = 0.375$ is caused by interference from second-order scattering processes. The error bars are standard deviations.

tions $V_1(\nu)$ and $V_2(\nu)$ are defined by

$$V_1(\nu) + iV_2(\nu) = \epsilon\nu^2 \left[1 - \epsilon\nu^2 \mathcal{P} \int \frac{g(\nu_0) d\nu_0}{\nu^2 - \nu_0^2} - \frac{1}{2} i\pi\epsilon\nu g(\nu) \right]^{-1}, \quad (2)$$

where $\epsilon = (M_H - M_I)/M_H$, M_H and M_I being the host and impurity masses ($\epsilon = -2.1$ for Au in Cu), \mathcal{P} denotes the principal value of the integral, and $g(\nu_0)$ is the frequency distribution for the host normalized to unity. (The M3 frequency distribution of Ref. 8 was used in the calculations.) For sufficiently small impuri-

ty concentrations, the frequency shifts and the widths of the line shapes for the alloy are given by

$$\Delta(\nu) = cV_1(\nu)/2\nu, \quad (3a)$$

and

$$\Gamma(\nu) = cV_2(\nu)/\nu. \quad (3b)$$

Equations (3) are, however, only valid in regions where $V_1(\nu)$ and $V_2(\nu)$ are slowly varying. "Better" values for Δ and Γ may be obtained directly from the $L(\nu, \nu_0)$.

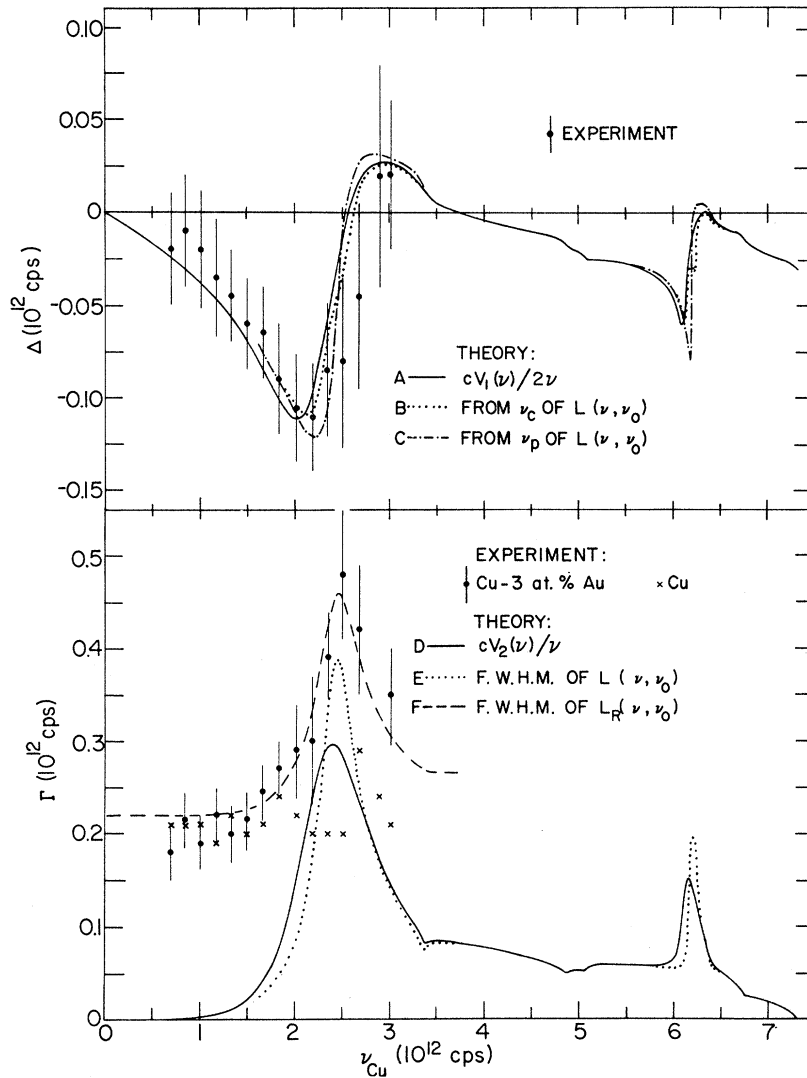


FIG. 2. Experimental frequency shifts, $\Delta = \nu_{\text{alloy}} - \nu_{\text{copper}}$, and neutron group widths, Γ , and calculated curves. ν_c and ν_p refer to the central frequencies at half-maximum and the peak frequencies, respectively. Curves A-E are for the idealized "perfect-resolution" case where the line shapes for the host are δ functions. Curve F includes the estimated experimental resolution (see text). The effect of resolution on the calculated curves for Δ is negligible with respect to the experimental accuracy.

If the $L(\nu, \nu_0)$ are folded with the appropriate resolution function, line shapes, $L_R(\nu, \nu_0)$, which are directly comparable with experiment may be obtained. Since one is primarily interested in the "extra" width of an alloy group, the appropriate resolution function can be taken to be the width (full width at half-maximum, FWHM) of the corresponding neutron group for the host crystal. The FWHM's of the neutron groups for copper were approximately constant (average about 0.22×10^{12} cps), so a Gaussian resolution function with this FWHM was used to calculate the resolution broadened line shapes, $L_R(\nu, \nu_0)$. Corresponding pairs of neutron groups are shown in Fig. 1 together with the appropriate $L_R(\nu, \nu_0)$ which have been drawn with the same peak heights and backgrounds as the alloy groups. Allowing for counting statistics, possible variations of the background, the probable errors in ν_0 (about ± 0.02), and the variations in the widths of the groups for copper (see Fig. 2), one sees that there is quite good agreement between calculated and measured line shapes.

The frequency shifts and the widths of the neutron groups for the alloy crystal are shown in Fig. 2 together with several curves calculated on the basis of the preceding theory. Good agreement is observed between the FWHM's of the $L_R(\nu, \nu_0)$ and the measured widths for the alloy. The errors assigned to the widths were determined from the shapes and statistics of the respective groups; they are possibly conservative estimates, but serve as a useful guide. The errors assigned to the experimental frequency shifts are the rms sums of the errors assigned to the corresponding frequencies for copper and for the alloy. These frequency shifts do not serve to discriminate between the various calculated curves (A, B, and C) [nor between these and similar curves calculated from the $L_R(\nu, \nu_0)$ but not shown]. However, the rise to the right of the negative peak in Δ appears to be less sharp than calculated, but much more sharp than that observed¹ for the Cu-9.3 at.% Au alloy. This suggests that the deviations from the calculated curves occur because the impurity concentrations are too large for the theory to be strictly applicable.

[Figure 2 also shows that, both theoretically and experimentally, the frequency at which Γ is a maximum is lower than the frequency at which $\Delta = 0$. Note also the discrepancies between the curves (A and D) given by Eqs.

(3) and the curves (B, C, and E) obtained directly from the $L(\nu, \nu_0)$.]

To sum up, the theory of Elliott and Maradudin seems almost adequate to explain the results for the Cu-3 at.% Au alloy, whereas it is definitely inadequate to explain the results¹ for the Cu-9.3 at.% Au alloy. The nature of the discrepancies between the calculated and experimental results in the two cases suggests that the impurity concentrations are too large for the (small-concentration) theory to apply. However, since the same branch was not studied at the two concentrations, it is not completely certain that this is the only limiting factor—force-constant changes (ignored by the theory) might be important as might also be short-range ordering in the high-concentration alloy. Further work on the Cu(Au) system, which may resolve these possibilities, is in progress.

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⁷J. M. Rowe, thesis, McMaster University, 1966 (unpublished).

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