Investigation of In-Band Resonant Modes in Cr-W Alloys by Inelastic Neutron Scattering*

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Transverse phonon groups in the [001] and [011] symmetry directions have been measured for Cr and three Cr-W alloys by inelastic neutron scattering using the triple-axis neutron diffractometer at the Missouri University Research Reactor. The tungsten concentration for the alloys are 0.3-, 0.8-, and 1.6-at.% W. The shifts in the phonon frequencies for each alloy showed the expected in-band resonant mode behavior. However, on extending the measurements of the shifts to the zone boundary in the [011] direction, additional structure was observed as well as a substantial increase in the magnitude of the negative shifts as one approaches the zone boundary. These frequency shifts are compared to the theory of Elliott and Maradudin using the frequency distribution function of chromium. The agreement between theory and experiment is no better for the lower tungsten concentrations than for previous results for Cr–3-at.% W. Thus, for the Cr-W system the mass-defect theory appears to be inadequate to predict the measured frequency shifts.

INTRODUCTION

The first significant theoretical work for determining the coherent inelastic neutron scattering by lattice vibrations of a crystal with substitutional defect impurities was presented by Elliot and Maradudin.[1] Experimental measurements to test this theory were first performed by Svensson and Brockhouse on Cu–9.3-at.% Au[2] and Cu–3-at.% Au,[3] and by Møller and Mackintosh on Cr–3-at.% W.[4] These measurements were made to observe the in-band resonance modes created by the substitution of a heavy mass defect into the host lattice.

The localized modes created by the substitution of a light mass defect into the host lattice were first observed by Nicklow *et al.* on Cu–4.1-at.% Al[5] and Cu–10-at.% Al.[6] Other measurements have been made on Ta–12-at.% Nb.[7]

The results of both Svensson and Brockhouse and Nicklow *et al.* indicate that the lower impurity concentrations are in much better agreement with the theory of Elliott and Maradudin. In addition, both authors felt that the discrepancy between theory and experiment for these lower impurity concentrations was due to force constant changes and/or too high an impurity concentration for the single-impurity theory.

Behera and Deo[8] have extended the theory of Elliott and Maradudin by including higher concentration-dependent terms. These additional concentration-dependent terms tend only to decrease the resonance frequency by a very small amount as the concentration is increased. Thus, they conclude that the discrepancy between the theory and experiment is not a concentration effect and suggest that experiments be performed with varying concentrations to see if a slight decrease in the resonance frequency occurs as predicted.

Behera and Deo[8] have also made calculations to examine the effect of force constant changes. Their results provide better qualitative agreement for W in Cr and Au in Cu, in that as the change in the force constants is increased, the amount of positive frequency shift decreases and the position of the maximum negative frequency shift increases to higher frequencies. However, they found that the magnitude of the theoretical frequency shift was too small. Other calculations[9] which consider changes in force constants have been made with results similar to the mass-defect model, but they are difficult to compare directly with experiment.

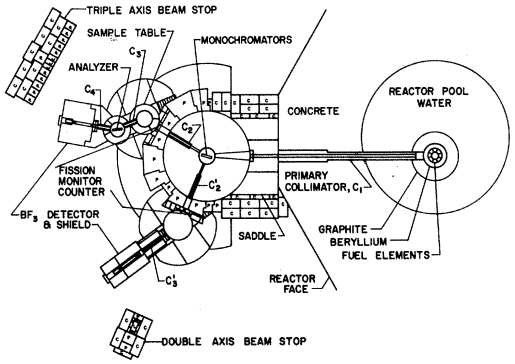

FIG. 1. Cutaway view of the MURR and dual-arm neutron diffractometer.

Since there is very poor agreement between the theory of Elliott and Maradudin and the results for Cr–3-at.% W, the present investigation of the in-band resonant modes in Cr-W alloys was undertaken to determine if better agreement could be obtained for lower tungsten concentrations as was the case for Cu-Au and Cu-Al. Further, the calculation used to compare the theory of Elliott and Maradudin to the

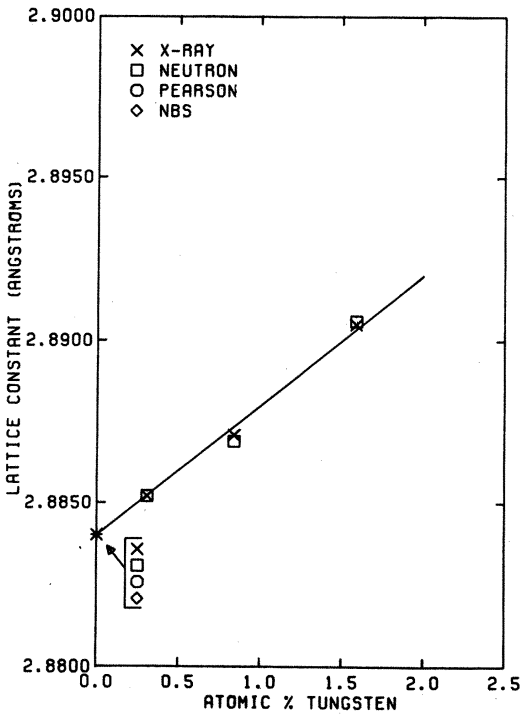

FIG. 2. Lattice constants of Cr and the Cr-W alloys.

experimental results of Møller and Mackintosh for Cr–3-at.% W was performed by Svensson[10] using a scaled tungsten frequency distribution function as an approximation to the frequency distribution for chromium. The present work used a frequency distribution function for chromium calculated by Feldman[11] in an attempt to remove a possible source of disagreement between theory and experiment. In addition, our results for varying concentrations would provide a check on the theory of Behera and Deo, as well as provide data which could be used to study changes in force constants.

THEORY

The differential scattering cross section for inelastic neutron scattering can be written as

$$d^2\sigma/d\Omega dE' = (1/4\pi\hbar)(k'/k_0)S(\mathbf{Q},\nu), \quad (1)$$

where k_0 and k' are the initial and final neutron wave vectors, and $S(\mathbf{Q},\nu)$ is the scattering function in terms of the momentum transfer $\hbar\mathbf{Q}$ and energy transfer $h\nu$. In the one-phonon coherent-scattering approximation, Elliott and Maradudin[1] have shown that the scattering function for the case of a heavy mass substitutional impurity can be written as

$$S(\mathbf{Q},\nu) = e^{-2W}\bar{a}^2 \sum_j [\mathbf{Q}\cdot\xi(\mathbf{q},j)]^2 L_j(\mathbf{q},\nu), \quad (2)$$

where e^{-2W} is the Debye-Waller factor, $\bar{a}$ is the average coherent-scattering length, and $\xi(\mathbf{q},j)$ is the polarization vector in terms of the phonon wave vector $\mathbf{q}$ and branch index j. The function $L_j(\mathbf{q},\nu)$ is given by

$$L_j(\mathbf{q},\nu) = \frac{cV_2(\nu)}{[\nu^2-\nu_0^2-cV_1(\nu)]^2+[cV_2(\nu)]^2}, \quad (3)$$

where c is the impurity concentration and ν_0 is the frequency of the normal mode of vibration for the host material. $V_1(\nu)$ and $V_2(\nu)$ are determined from the equation

$$V_1(\nu)+iV_2(\nu)$$

$$= \epsilon\nu^2\{1-\epsilon\nu^2 P\int[G(\nu_0)d\nu_0/(\nu^2-\nu_0^2)]-i\tfrac{1}{2}\pi\epsilon G(\nu)\}^{-1}, \quad (4)$$

where $G(\nu_0)$ is the frequency distribution function for the host material, P indicates that the principal value of the integral should be taken, and ϵ is the mass-defect parameter defined by $\epsilon=(M-M')/M$, where M is the mass of the host atom and M' is the mass of the impurity atom.

Since $L_j(\mathbf{q},\nu)$ is essentially Lorentzian in shape, the frequency shift in the peak position is given by

$$\Delta = \nu - [\nu^2 - cV_1(\nu)]^{1/2}. \quad (5)$$

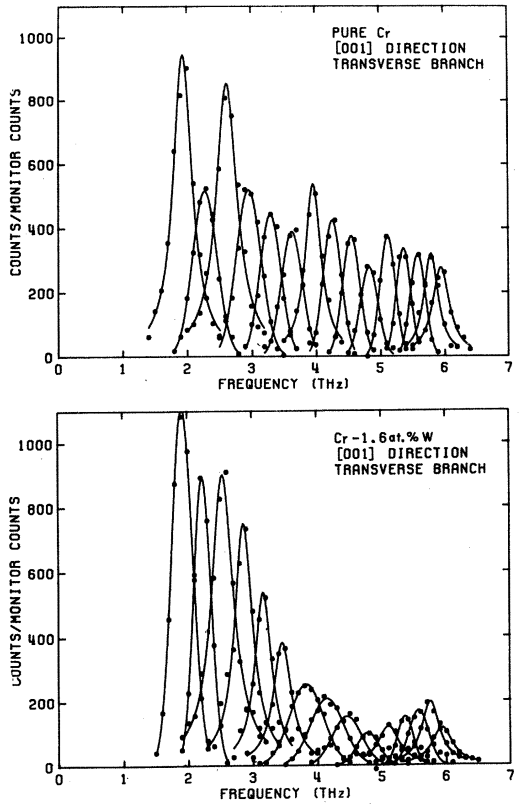

FIG. 3. Representative transverse neutron groups for Cr and Cr–1.6-at.% W with background subtracted. The solid lines were obtained by a least-squares fit to Gaussian or Lorentzian functions. The neutron groups for Cr are not normalized to the same number of monitor counts.

For small concentrations and if $V_1(\nu)$ and $V_2(\nu)$ are slowly varying functions of ν, then the frequency shift is given by

$$\Delta = cV_1(\nu)/2\nu. \tag{6}$$

MEASUREMENTS

The data for this investigation were taken on the triple-axis unit of the dual-arm neutron diffractometer[12] located at the 5-MW Missouri University Research Reactor (MURR). A cutaway drawing of the reactor and diffractometer are shown in Fig. 1. Zinc crystals which were oriented for the (0002) Bragg reflection were used as the monochromator and analyzer crystals on the triple-axis unit. The neutron flux at the sample table is approximately 2×10^6 n/cm^2 sec.

Four single crystals were used for this investigation: Cr, Cr–0.3-at.% W, Cr–0.8-at.% W, and Cr–1.6-at.% W. These crystals, which are approximately $1\frac{1}{2}$ in. long and $\frac{3}{8}$ in. in diameter, were purchased from the Ames Laboratory, U. S. A.E.C., Iowa State University, Ames,

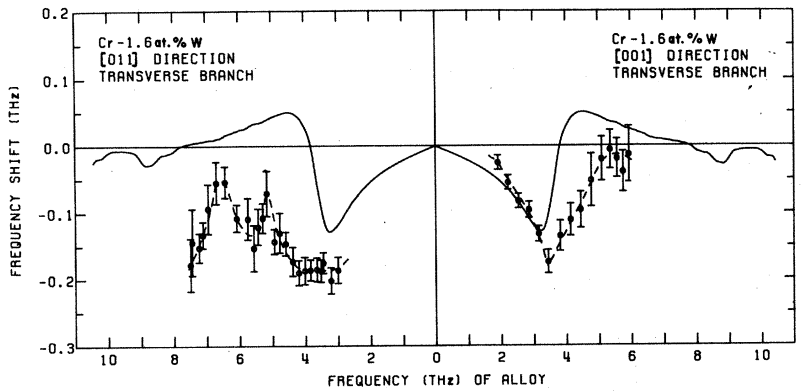

FIG. 4. Frequency shifts as a function of the frequency of the alloy for Cr–1.6-at.% W. The solid line represents a calculation using Eq. (6). The dotted line has been drawn as a guide through the data points.

Iowa. The concentration for each alloy was determined by spectroscopic analysis and the lattice constants were determined by x-ray powder techniques and by elastic neutron scattering. The results of these measurements are shown in Fig. 2 along with comparisons of previous results recorded by the National Bureau of Standards[13] and Pearson.[14] The "constant-Q"[15] method was used to measure the neutron groups about the (020) and (022) reciprocal-lattice points for the [001] direction and the [011] direction, respectively.

Figure 3 shows representative transverse neutron groups for Cr and Cr–1.6-at.% W in the [001] direction after background corrections were made. The solid lines drawn through the corrected data points are a least-squares fit to either a Gaussian or Lorentzian function. The individual neutron groups for Cr are not normalized to the same number of monitor counts because the phonon intensities decrease significantly with increasing wave vector. Numerical values corresponding to the data points for Cr are listed in Table I.

TABLE I. Measured reduced phonon wave vectors ζ with corresponding frequencies ν_0 for Cr.

$T[0\zeta\zeta]$		$T[00\zeta]$	
ζ	ν_0 (THz)	ζ	ν_0 (THz)
0.150	3.179±0.011	0.150	1.940±0.006
0.160	3.414±0.009	0.175	2.280±0.005
0.170	3.619±0.005	0.200	2.621±0.005
0.175	3.704±0.005	0.225	2.960±0.006
0.180	3.825±0.005	0.250	3.279±0.006
0.190	4.020±0.006	0.275	3.631±0.007
0.200	4.193±0.004	0.300	3.962±0.006
0.210	4.379±0.006	0.325	4.257±0.005
0.220	4.549±0.004	0.350	4.552±0.007
0.225	4.648±0.006	0.375	4.833±0.008
0.230	4.730±0.005	0.400	5.120±0.007
0.240	4.900±0.006	0.425	5.366±0.007
0.250	5.073±0.007	0.450	5.589±0.008
0.260	5.232±0.007	0.475	5.792±0.009
0.270	5.396±0.008	0.500	5.949±0.011
0.280	5.549±0.008		
0.290	5.715±0.010		
0.300	5.849±0.007		
0.325	6.181±0.007		
0.350	6.482±0.013		
0.375	6.748±0.019		
0.400	7.046±0.021		
0.425	7.242±0.012		
0.450	7.407±0.017		
0.475	7.586±0.024		
0.500	7.666±0.011		

RESULTS

The frequency shifts, $\Delta=\nu-\nu_0$, where ν is the frequency of a neutron group in the alloy and ν_0 is the frequency of a corresponding neutron group in the host, are plotted in Fig. 4 for Cr–1.6-at.% W and in Fig. 5 for Cr–0.3-at.% W as a function of the frequency of the alloy for the [001] and [011] directions. The solid lines in Figs. 4 and 5 represent the theoretical frequency shifts obtained from Eq. (6) using Eq. (4) to calculate the functions $V_1(\nu)$ and $V_2(\nu)$. The frequency distribution function for chromium used in the calculation was based on the work of Feldman.[11] The dashed lines in Figs. 4 and 5 are arbitrarily drawn through the data. For each alloy the error bars correspond to twice the sum of the standard deviations from the peak positions of the host and alloy neutron groups.

For each symmetry direction the neutron groups for all of the samples were measured from the same reciprocal-lattice point and with the same instrumental configuration. Hence for a specific symmetry direction and a particular momentum transfer the instrumental resolution would be essentially the same for the corresponding neutron group of each sample. Thus no resolution corrections are necessary for the shifts in the peak positions.

An examination of Figs. 4 and 5 shows that although the theory predicts reasonably well the over-all magnitudes of the frequency shifts, there are some notable discrepancies. First, the theory, which does not consider changes in force constants, is branch independent while the experimental frequency shifts are observed to be different for the two symmetry directions. Thus there is better agreement between theory and experiment in the [001] direction than in the [011] direction. Second, in both concentrations there are no observed positive frequency shifts as predicted by the theory. Third, if the discrepancy between the theory and experiment for Cr–1.6-at.% W is entirely due to the effects of a high

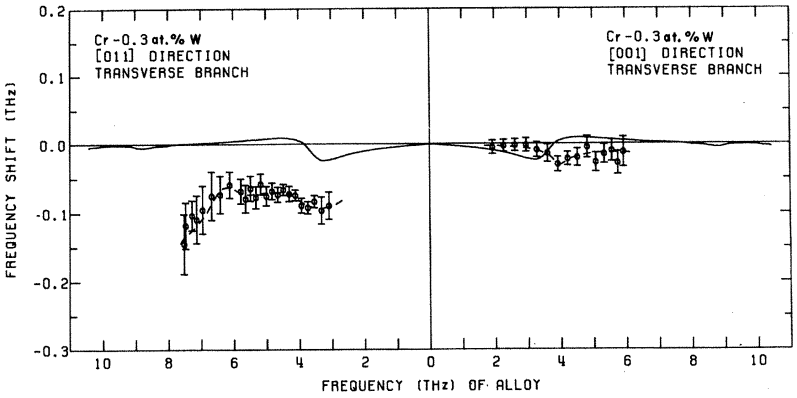

FIG. 5. Frequency shifts as a function of the frequency of the alloy for Cr–0.3-at. % W. The solid line represents a calculation using Eq. (6). The dotted line has been drawn as a guide through the data points.

impurity concentration, then there should be better agreement for the 0.3-at.% W concentration. However, the agreement between theory and experiment appears to be no better for the lower tungsten concentration, indicating that the discrepancy is not predominately due to concentration effects.

Recent theories[9,16] which consider force constant changes have shown that the cross section for coherent inelastic neutron scattering has an explicit dependence on the phonon wave vector and branch index. Thus, in Fig. 6 we have plotted the frequency shifts as a function of the reduced wave vector, $\zeta = qa/2\pi$. The data points corresponding to Fig. 6 are tabulated in Table II.

Previous investigators have measured the frequency shifts only about halfway to the zone boundary. However, we have extended our results to the zone boundary in the [011] direction as shown in Fig. 6. In this figure additional structure can be observed in the region $0.3<\zeta<0.4$ as well as an increase in the frequency shifts as one approaches the zone boundary. A comparison of the data also reveals the same type of structure for each concentration, but with a reduction in the magnitude of the frequency shifts as the concentration is decreased. In the [001] direction one can see that the effect of decreasing the concentration is mainly a reduction in the magnitude of the negative shifts with a slight increase of the maximum negative frequency shift to a higher frequency as predicted by Behera and Deo. In the [011] direction the result of decreasing the concentration is again a reduction in the magnitude of the frequency shifts. In this case the peaks in the shifts seem to move to lower frequencies as the concentration is decreased.

CONCLUSION

The experimental results have indicated that the agreement between theory and experiment for the Cr-W alloys is not significantly improved by decreasing the impurity concentration to as low as 0.3-at.% W. In addition the experimental frequency shifts are branch dependent, show added structure, and increase significantly toward the zone boundary. Thus, for the Cr-W system with an impurity concentration as low as

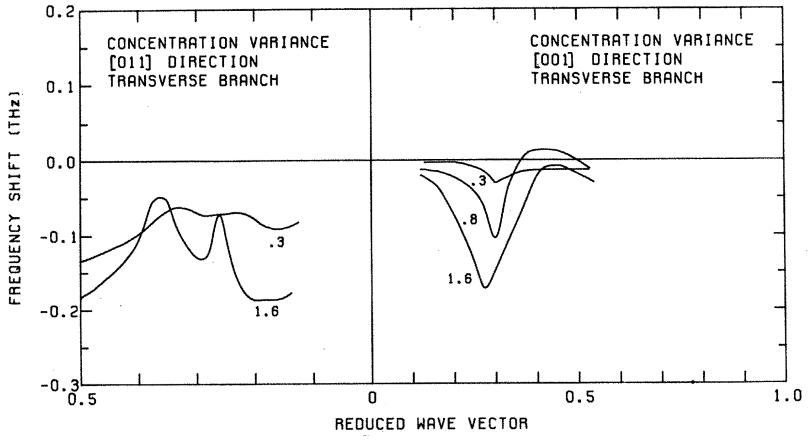

FIG. 6. Frequency shifts as a function of the reduced phonon wave vector ζ for the measured concentrations.

TABLE II. Measured reduced phonon wave vectors ζ with corresponding frequencies ν and frequency shifts $\Delta\nu$ for the three Cr-W alloys.

$T[0\zeta\zeta]$			$T[00\zeta]$		
ζ	ν (THz)	$\Delta\nu$	ζ	ν (THz)	$\Delta\nu$
	Cr–0.3-at.% W			Cr–0.3-at.% W	
0.150	3.090±0.009	−0.089±0.020	0.150	1.935±0.004	−0.005±0.010
0.160	3.318±0.011	−0.096±0.020	0.175	2.277±0.004	−0.003±0.009
0.170	3.536±0.004	−0.083±0.009	0.200	2.619±0.004	−0.002±0.009
0.180	3.733±0.004	−0.092±0.009	0.225	2.958±0.004	−0.002±0.010
0.190	3.931±0.005	−0.089±0.011	0.250	3.288±0.005	−0.009±0.011
0.200	4.119±0.004	−0.074±0.008	0.275	3.617±0.006	−0.014±0.013
0.210	4.307±0.005	−0.072±0.011	0.300	3.932±0.005	−0.030±0.011
0.220	4.483±0.004	−0.066±0.008	0.325	4.235±0.055	−0.022±0.010
0.230	4.657±0.006	−0.073±0.011	0.350	4.532±0.006	−0.020±0.013
0.240	4.832±0.006	−0.068±0.012	0.375	4.828±0.008	−0.005±0.016
0.250	4.998±0.007	−0.075±0.014	0.400	5.093±0.007	−0.027±0.014
0.260	5.174±0.008	−0.058±0.015	0.425	5.351±0.007	−0.015±0.014
0.270	5.319±0.008	−0.077±0.016	0.450	5.579±0.008	−0.010±0.016
0.280	5.485±0.010	−0.064±0.018	0.475	5.764±0.008	−0.028±0.017
0.290	5.636±0.010	−0.079±0.020	0.500	5.937±0.011	−0.012±0.022
0.300	5.781±0.011	−0.068±0.018		Cr–0.8-at.% W	
0.325	6.122±0.012	−0.059±0.019	0.150	1.937±0.012	−0.003±0.018
0.350	6.409±0.014	−0.073±0.027	0.175	2.244±0.013	−0.036±0.018
0.375	6.673±0.016	−0.075±0.035	0.200	2.610±0.016	−0.011±0.021
0.400	6.951±0.014	−0.095±0.035	0.225	2.930±0.011	−0.030±0.017
0.425	7.133±0.023	−0.109±0.035	0.250	3.254±0.019	−0.043±0.025
0.450	7.275±0.011	−0.132±0.028	0.275	3.571±0.022	−0.060±0.029
0.475	7.468±0.010	−0.118±0.034	0.300	3.858±0.025	−0.104±0.031
0.500	7.521±0.033	−0.145±0.044	0.325	4.207±0.027	−0.050±0.032
	Cr–1.6-at.% W		0.350	4.533±0.032	−0.019±0.039
0.150	2.993±0.009	−0.186±0.020	0.375	4.850±0.044	0.017±0.052
0.160	3.212±0.011	−0.202±0.020	0.400	5.130±0.026	0.010±0.033
0.170	3.444±0.011	−0.175±0.016	0.425	5.391±0.030	0.025±0.037
0.175	3.517±0.012	−0.187±0.017	0.450	5.550±0.029	−0.039±0.037
0.180	3.640±0.013	−0.185±0.018	0.475	5.776±0.025	−0.016±0.034
0.190	3.834±0.010	−0.186±0.016	0.500	6.004±0.042	0.055±0.053
0.200	4.006±0.017	−0.187±0.021		Cr–1.6-at.% W	
0.210	4.189±0.013	−0.190±0.019	0.150	1.915±0.005	−0.025±0.011
0.220	4.376±0.018	−0.173±0.022	0.175	2.225±0.006	−0.055±0.011
0.230	4.584±0.013	−0.146±0.018	0.200	2.538±0.006	−0.083±0.011
0.240	4.770±0.024	−0.130±0.030	0.225	2.864±0.006	−0.096±0.012
0.250	4.930±0.012	−0.143±0.019	0.250	3.165±0.007	−0.132±0.012
0.260	5.161±0.027	−0.071±0.034	0.275	3.457±0.011	−0.174±0.018
0.270	5.288±0.014	−0.108±0.022	0.300	3.827±0.017	−0.135±0.023
0.280	5.428±0.019	−0.121±0.027	0.325	4.146±0.019	−0.111±0.024
0.290	5.562±0.025	−0.153±0.035	0.350	4.456±0.020	−0.096±0.027
0.300	5.740±0.024	−0.109±0.031	0.375	4.781±0.032	−0.052±0.040
0.325	6.073±0.013	−0.108±0.020	0.400	5.100±0.026	−0.020±0.033
0.350	6.428±0.011	−0.054±0.024	0.425	5.360±0.022	−0.006±0.029
0.375	6.693±0.013	−0.055±0.032	0.450	5.570±0.021	−0.019±0.029
0.400	6.952±0.016	−0.094±0.037	0.475	5.753±0.022	−0.039±0.031
0.425	7.109±0.008	−0.133±0.020	0.500	5.936±0.031	−0.031±0.042
0.450	7.226±0.011	−0.181±0.028			
0.475	7.442±0.026	−0.144±0.050			
0.500	7.488±0.029	−0.178±0.040			

0.3-at.% W the mass-defect theory is inadequate to predict the measured frequency shifts. Rather the results suggest that a more complex theory which includes changes in force constants will be necessary to explain the details of the experimental data.

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