IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Vibrational spectra of quasi-periodic metallic superlattices

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 7689

(http://iopscience.iop.org/0953-8984/1/41/021)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.96
The article was downloaded on 10/05/2010 at 20:32

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 1 (1989) 7689–7694. Printed in the UK

# Vibrational spectra of quasi-periodic metallic superlattices

Xia Hua and Zhang Xing-Kui
Laboratory of Solid State Microstructures, University of Nanjing, Nanjing, Jiangsu, People's Republic of China

Received 29 July 1988, in final form 23 March 1989

**Abstract.** Raman scattering studies of several Cu/Nb quasi-periodic metallic superlattices fabricated by the magnetron sputtering technique are presented. The obtained room-temperature vibrational spectra of superlattice phonons were analysed using an elastic continuum model. For quasi-periodicity below about 5.0 nm a resonant-like TA phonon spectrum corresponding to the 514.5 nm excited line is observed, but the dominant Raman spectral feature of quasi-periodicity greater than about 14.0 nm resembles folded acoustic modes in periodic metallic superlattices. The calculation of the theoretical frequencies shows good agreement with the experimental data.

Since the success of artificially fabricating one-dimensional quasi-periodic GaAs–AlAs (Merlin *et al* 1985), considerable effort has been devoted to investigating its vibrational properties both theoretically (Nori and Rodriguez 1986, Dharma-Wardana *et al* 1987) and experimentally (Nakayama *et al* 1987, Bajema and Merlin 1987). Raman scattering permits us to probe the vibrational properties of the periodic superlattice, e.g. the zone folding effect due to acoustic wave propagation in the periodic layered media. For the quasi-periodic superlattice, the phonon spectrum is similar to that of folded acoustic modes in the periodic superlattice, but the folded doublet peaks at non-equal intervals. The resonant scattering of quasi-periodic superlattices shows a weighted density of states, revealing the expected rich structure of major gaps in the phonon spectrum. In recent years, much attention has been paid to the quasi-periodic metallic superlattice (Hu *et al* 1986, Zhang *et al* 1988, Xia *et al* 1989). The results obtained from Brillouin scattering show little difference between the elastic properties of periodic metallic superlattices and those of quasi-periodic lattices. The observation of folded acoustic modes in metallic superlattices (Zhang *et al* 1989) has encouraged us to study the vibrational properties of the quasi-periodic metallic superlattice. In the present paper, following our previous work, we present some new experimental results on the acoustic vibrational properties of quasi-periodic metallic Cu/Nb superlattices over the quasi-periodicity range 4.74–20.56 nm using two different incident excited lines (488.0 and 514.5 nm). All data are interpreted in terms of a well known elastic continuum model, and the model seems to explain the main features of the Raman spectra satisfactorily.

The goals of the present study were to explore, quantitatively, the vibrational properties of low-frequency acoustic phonons in quasi-periodic metallic superlattices following investigation of surface phonons by Brillouin spectroscopy. Secondly, in view

0953-8984/89/417689 + 06 $02.50 © 1989 IOP Publishing Ltd

**Table 1.** The results of experimental and calculated frequencies and intensities of the folded doublets. The Brillouin frequencies are 2 cm$^{-1}$ for samples 3 and 4, and 2.5 cm$^{-1}$ for sample 5.

| Sample | $(m, n)$ | $\omega_{calc}$ (cm$^{-1}$) | $\omega_{exp}$ (cm$^{-1}$) | $I_{calc}$ | $I_{exp}$ |
|---|---|---|---|---|---|
| 3 | (1, 0) | 9.58 | — | 0.344 | — |
| 3 | (1, 0) | 13.6 | — | 0.343 | — |
| 3 | (0, 1) | 16.7 | 17.5 | 0.612 | 0.612 |
| 3 | (0, 1) | 20.7 | 21.5 | 0.611 | 0.611 |
| 3 | (1, 1) | 28.3 | 27.5 | 1.681 | 0.426 |
| 3 | (1, 1) | 32.3 | 32.0 | 1.680 | 0.322 |
| 3 | (0, 2) | 35.4 | 35.5 | 0.013 | 0.319 |
| 3 | (0, 2) | 39.4 | 38.5 | 0.013 | 0.333 |
| 3 | (2, 1) | 39.9 | 40.5 | 0.118 | 0.335 |
| 3 | (2, 1) | 43.9 | 44.0 | 0.118 | 0.158 |
| 3 | (3, 1) | 51.4 | 51.5 | 0.065 | 0.204 |
| 3 | (3, 1) | 55.4 | 55.5 | 0.065 | 0.198 |
| 4 | (1, 0) | 6.28 | — | 1.075 | — |
| 4 | (1, 0) | 10.3 | — | 1.068 | — |
| 4 | (0, 1) | 11.4 | — | 3.368 | — |
| 4 | (0, 1) | 15.4 | — | 3.360 | — |
| 4 | (1, 1) | 19.7 | 21.0 | 4.487 | 4.487 |
| 4 | (1, 1) | 24.7 | 25.0 | 4.483 | 4.483 |
| 4 | (4, 0) | 31.1 | 30.5 | 0.009 | 4.192 |
| 4 | (1, 2) | 33.1 | — | 1.710 | — |
| 4 | (4, 0) | 35.1 | 36.0 | 0.008 | 3.445 |
| 4 | (1, 2) | 37.1 | — | 1.709 | — |
| 4 | (2, 2) | 41.4 | 42.0 | 0.319 | 0.556 |
| 4 | (2, 2) | 45.4 | 45.0 | 0.319 | 0.537 |
| 4 | (3, 2) | 49.6 | 48.0 | 0.002 | 0.407 |
| 4 | (3, 2) | 53.6 | 53.0 | 0.002 | 0.352 |
| 5 | (1, 0) | 11.2 | — | 0.693 | — |
| 5 | (1, 0) | 16.2 | — | 0.691 | — |
| 5 | (0, 1) | 19.7 | 20.0 | 1.641 | 1.641 |
| 5 | (0, 1) | 24.7 | 25.5 | 1.639 | 1.639 |
| 5 | (1, 1) | 33.4 | 33.0 | 3.285 | 1.436 |
| 5 | (1, 1) | 38.4 | 38.0 | 3.283 | 0.940 |
| 5 | (3, 0) | 38.7 | 38.0 | 0.002 | 0.900 |
| 5 | (3, 0) | 43.7 | 43.0 | 0.002 | 0.701 |
| 5 | (2, 1) | 47.2 | 46.5 | 0.077 | 0.598 |
| 5 | (2, 1) | 52.2 | 52.0 | 0.077 | 0.570 |
| 5 | (1, 2) | 55.7 | 55.0 | 1.545 | 0.445 |
| 5 | (1, 2) | 60.7 | 60.0 | 1.543 | 0.393 |

of the question of opacity of metallic superlattices, the use of light scattering was indicated since it is a non-destructive technique which allows acoustic vibrational modes to be probed even though the penetration of light is less than 300–400 nm.

All samples used in this study were prepared by the magnetron sputtering technique. $SiO_2$ glass wafers were employed as the substrate. The quasi-periodic Cu/Nb metallic superlattices prepared involve two distinct 'building blocks' A and B and they are ordered in a Fibonacci sequence (Levine and Steinhardt 1984). The building blocks are composed of two layers and have arbitrary thicknesses $d_A \neq d_B$, and their $d_A/d_B$ is less than the golden mean $\tau$ ( = $(1 \pm 5)/2$); thus $d = (\tau d_A + d_B)$ describes the average lattice constant of the Fibonacci superlattice. The total thicknesses of our samples vary between 1.8 and 2.5 $\mu$m. In this case, the laser light will be substantially attenuated before it strikes the substrate. Because large-angle x-ray diffraction peaks are in agreement with the theoretical values, we are convinced that the preferred growth planes with respect to Cu and Nb sublayers are, respectively, (111) and (110) (Hu *et al* 1986).

Light from an argon ion laser was used to illuminate the samples. Scattering light was analysed with a double monochromator and detected with a photomultiplier tube operated in the photon-counting mode. A Datamate system was used to collect the data and to control the experiment. All measurements were performed with light incident in a back-scattering geometry, polarised parallel to the surface of the sample.

For the superlattice system formed according to the Fibonacci sequence, in the limit of long wavelengths and low frequencies, each sublayer can be treated as an elastic medium. We consider phonons with wavevectors perpendicular to interfaces. By assuming decoupling between different phonon modes, we denote by $U^l(j, z)$ and $U^t(j, z)$ the non-vanishing displacement components of longitudinal and transverse lattice vibrations in the $j$th sublayer. The elastic continuum model expressions for phonon frequencies in quasi-periodic superlattices are determined by solving the wave equations

$$\partial^2 U^l(j, z)/\partial t^2 = [v^l(j, z)]^2 \, \partial^2 U^l(j, z)/\partial z^2 \qquad (1)$$

and

$$\partial^2 U^t(j, z)/\partial t^2 = [v^t(j, z)]^2 \, \partial^2 U^t(j, z)/\partial z^2 \qquad (2)$$

where $v^l(j, z)$ and $v^t(j, z)$ are the local velocities of sound of the longitudinal and transverse acoustic waves propagating in the $j$th sublayer along the superlattice growth axis $z$. Also they are constant in each sublayer (i.e. in the Cu and Nb layer). The two constituents of the Cu/Nb superlattices are composed of cubic sublayers with their [111] and [110] axes oriented along the axis of the superlattice. The solutions of the wave equations must satisfy boundary conditions at the different interfaces and at the free surface. It follows from equations (1) and (2) that the Raman frequency $\omega^{\pm}(m, n)$ and intensity $I[\omega^{\pm}(m, n)]$ (Merlin *et al* 1985, Dharma-Wardana *et al* 1987) are given by

$$\omega^{\pm}(m, n) = |k(m, n) \pm q| V_{\rm eff} \qquad (3)$$

and

$$I[\omega^{\pm}(m, n)] \propto \{n[\omega^{\pm}(m, n)] + 1\} S(m, n) |P(m, n)|^2 / \omega^{\pm}(m, n) \qquad (4)$$

where

$$k(m, n) = 2\pi(m + \tau n)/(\tau d_A + d_B) \qquad (5)$$

and the structure factor $S(m, n)$ of the Raman spectrum for the quasi-periodic superlattice is

$$S(m, n) \propto \left| \frac{2\tau^2 \sin[k(m, n) d_B/d] \sin[\pi\tau^2 (m d_A/d_B - n) d_B/d]}{\pi\tau^2 k(m, n) d_B (m d_A/d_B - n)} \right|^2 . \qquad (6)$$

Here $V_{\rm eff}$ is the effective velocity of sound in the superlattice, $P(m, n)$ is the Fourier component of the photoelastic constant with wavevector $k(m, n)$, and $n[\omega^{\pm}(m, n)] + 1$ is the thermal factor. The parameters in equations (3)–(6) are labelled by the quasi-periodicity indices $(m, n)$, where $m$ and $n$ span all integers.

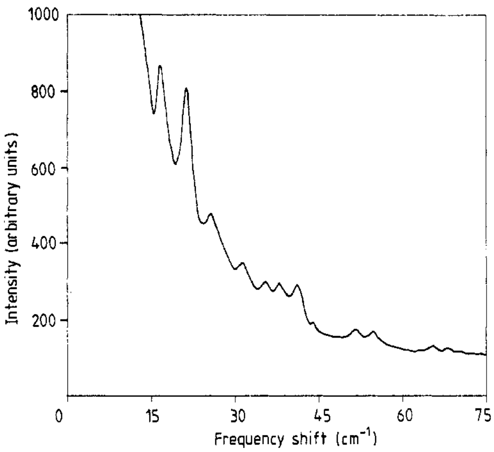


**Figure 1.** Raman spectrum of the Cu/Nb quasi-periodic metallic superlattice for sample 3 with average lattice constant $d = 14.74$ nm (laser wavelength $\lambda = 488.0$ nm; $T = 290$ K).

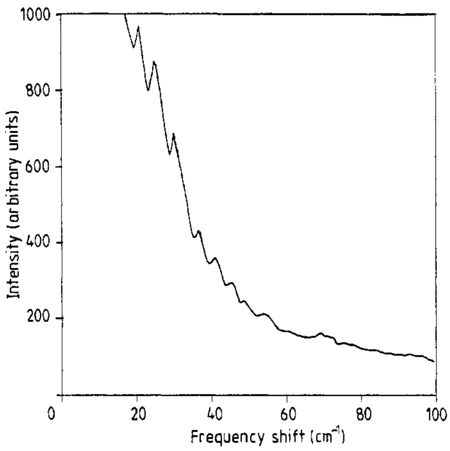


**Figure 2.** Raman spectrum of the Cu/Nb quasi-periodic metallic superlattice for sample 4 recorded for an excitation wavelength of 514.5 nm ($T = 290$ K).

The effective longitudinal or transverse velocity of sound in the Cu/Nb quasi-periodic superlattice can be estimated simply from the density and the thickness average of the constituent velocities. For the Cu/Nb quasi-periodic superlattice, as mentioned above, the growth directions are [111] for Cu sublayers and [110] for Nb sublayers, respectively. On the basis of simple calculations, we found that the effective longitudinal and transverse velocities of sound in the Cu/Nb quasi-periodic superlattice are $5.10 \pm 0.10$ km s$^{-1}$ and $2.10 \pm 0.10$ km s$^{-1}$. The Brillouin frequency $qV_{\text{eff}}$, in fact, is uncertain because of the poorly known refractive index of the Cu/Nb metallic superlattice, but the results of calculation indicate that it varies between 2 and 3 cm$^{-1}$ for several samples with different quasi-periodicities.

Figure 1 displays the Raman spectrum of a Cu/Nb quasi-periodic superlattice in the frequency region of acoustic phonons. The sharp doublets, which originate from the folding of longitudinal acoustic phonons, are similar to the Raman profiles of the folded acoustic modes in periodic superlattices (Zhang *et al* 1989). The positions of weak peaks, for the region of frequency shift greater than 22 cm$^{-1}$, can be labelled by the quasi-periodicity indices $(m, n)$ but their profiles and intensities are broadened and decreased, respectively. In general, peak broadening could be accounted for because of uncertainty in the wavevector $q$ due to the opacity of the metallic films. However, the relative intensities of folded doublets are apparently different. Figure 2 shows a further example of the folded acoustic modes in the quasi-periodic Cu/Nb superlattice for sample 4 whose average lattice constant is 20.56 nm. One feature of Raman spectrum is that the folded doublets appear only below the frequency region of 30 cm$^{-1}$, and spectral profiles for frequencies greater than 30 cm$^{-1}$ are analogous to those produced by resonant-like scattering.

The experimental and theoretical results are given in table 1. The calculated values agree fairly well with the observed positions of the Raman peaks. Although the absolute scattering intensity of the Raman peak is not predicted only according to equation (4), the relative intensity of the folded doublet could be scaled to that of the calculated spectrum. During the computed simulation procedure, the measured peak intensity was

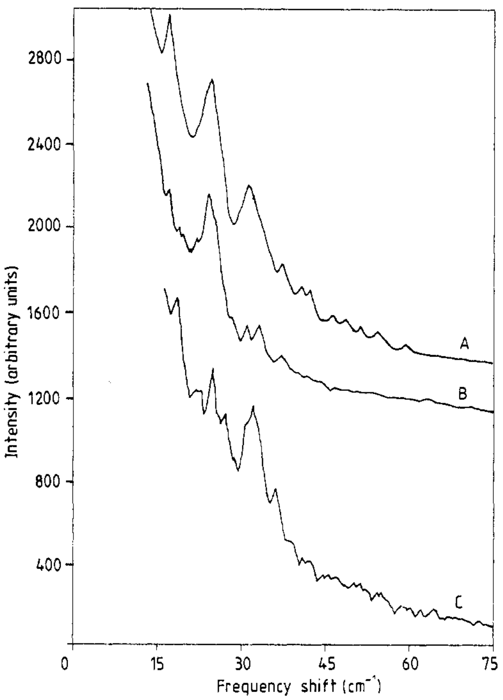


**Figure 3.** Raman spectra of two amorphous quasi-periodic metallic superlattices for sample 5 (curve A) and sample 6 (curves B and C) with smaller quasi-periodicity $d = 4.74$ nm. Spectra A and B are excited by the 488.0 nm line and spectrum C by the 514.5 nm line.

scaled to the calculated peak intensity at 21.5 cm$^{-1}$ for sample 3 and at 21.0 cm$^{-1}$ for sample 4. The calculated relative scattering intensity $I_{calc}$ that we found did not agree with the experimental intensity $I_{exp}$.

For shorter quasi-periodicity samples, the regular lattice structure in the sublayers may be lost owing to a fluctuation of the individual thicknesses of building blocks A and B as well as to island growth etc. X-ray diffraction patterns indicated that, when the individual thickness $d_A$ or $d_B$ is less than 2.0 nm, the superlattices will be amorphous. In order to study the vibrational properties of the amorphous quasi-periodic metallic superlattices, we also studied the Raman scattering of the average lattice constant $d < 5.0$ nm for the Cu/Nb quasi-periodic superlattice. The building blocks of sample 5 are A ≡ [1.0 nm Cu, 1.0 nm Nb], B ≡ [1.0 nm Cu, 0.5 nm Nb], and those of sample 6 are A ≡ [1.0 nm Cu, 1.0 nm Nb], B ≡ [0.5 nm Cu, 1.0 nm Nb]. In figure 3, we present the Raman spectra of samples 5 and 6 recorded under excitation lines of wavelengths 488.0 and 514.5 nm. Curve A shows the Raman spectrum of sample 5 and the doublets can be seen clearly but the relative intensities of the folded doublets are more unequal in this sample with smaller quasi-periodicity. Curves B and C correspond to the Raman spectra of sample 6 for two laser wavelengths. Although the peak positions in the spectrum excited by the 488.0 nm wavelength correspond to the folded doublets of sample 5, the Raman spectrum of sample 6 excited by the 514.5 nm wavelength again seems to be analogous to near-resonant scattering (Merlin *et al* 1985, Bajema and Merlin 1987). The results of calculation show that the folded doublets of samples 5 and 6 are due to the folding of the transverse acoustic modes, and the experimental and theoretical values for sample 5 are also shown in table 1.

In the Raman spectra shown in figures 1–3, the scattering intensity is enhanced by the thermal factor $n[\omega^{\pm}(m, n)] + 1$. Therefore, when the relative intensities of Raman peaks are interpreted, one must consider this factor. Of course, we cannot determine at present whether Raman spectra are near-resonant or non-resonant scattering because we used only two discrete excitation wavelengths of an $Ar^+$ ion laser. However, an assumptive interpretation for the quasi-periodic Cu/Nb superlattice is that the non-resonant and near-resonant scattering both make some contribution to the vibrational spectra of the metallic superlattices. The detailed theoretical considerations will be presented elsewhere.

In summary, we have shown that Raman spectroscopy provides insight into the vibrational properties of the Cu/Nb quasi-periodic metallic superlattices. The elastic continuum model predicts the frequencies for the folded acoustic modes well. The vibrational spectra for the 488.0 nm excited wavelength may be consistent with the profiles of the non-resonant scattering, but we cannot definitely assign them to resonant or non-resonant scattering at present. If one considers further the high absorption of metal materials and the coupling between electrons and phonons within the framework of the elasticity theory, the scattering intensity in this quasi-periodic superlattice is able to be predicted.

## Acknowledgment

This work was supported by the Laboratory of Solid State Microstructures of Nanjing University.

## References

Bajema K and Merlin R 1987 *Phys. Rev.* B **36** 4555
Dharma-Wardana M W C, MacDonald A T, Lockwood D J, Baribeau J M and Houghton D C 1987 *Phys. Rev. Lett.* **58** 1761
Hu A, Tien C, Li X-J, Wang Y-H and Feng D 1986 *Phys. Lett.* **119A** 313
Levine D and Steinhardt P J 1984 *Phys. Rev. Lett.* **53** 2477
Merlin R, Bajema K, Clarke R, Juang F Y and Bhattacharya P K 1985 *Phys. Rev. Lett.* **55** 1768
Nakayama M, Kato H and Nakashima S 1987 *Phys. Rev.* B **36** 3472
Nori F and Rodriguez J P 1986 *Phys. Rev.* B **34** 2207
Xia H, Zhang X-K, Hu A, Zhang W, Zhu S-N and Tien C 1989 *Phys. Status Solidi* **110** 99
Zhang X-K, Xia H, Hu A, Zhang M-S, Yuan X-Y, Qian C and Zhu S-N 1989 *Mod. Phys. Lett.* B **3** 381
Zhang X-K, Xia H, Hu A and Zhu S-N 1988 *Chin. Phys. Lett.* **5** 377