

harmful to the applicability of this method to cases involving mosaic crystals, since mosaic crystals are composed of many tiny perfect crystal blocks. Strong primary or secondary reflections are still suitable for phase determinations from mosaic crystals. Application of this method has recently been applied to the monoclinic crystal of $\text{Cs}_{10}\text{Ga}_8\text{Se}_{14}$. The determination of this structure has been attempted by the ordinary direct method, for example, the MULTAN program,¹² but without success. By use of the present method, fourteen phase angles were obtained from fourteen triplet phase relations via Eq. (1). By treating these phase angles as the starting phases for the program MULTAN74, we were able to determine the relative positions of Cs, Ga, and Se in the unit cell. This is the first application of multiple diffraction to crystal-structure determination. For more complicated, for example, noncentrosymmetric crystals, Eq. (1) will still be valid. However, S_L for random phases, between 0° and 360° , will be more complicated and more difficult to handle than the centrosymmetric cases.

The author is indebted to Professor H.-J. Queisser of the Max-Planck-Institute for encouragement and useful discussions. The critical read-

ing of this manuscript by Dr. B. Fischer is also gratefully acknowledged.

(a) On leave from Instituto de Física, Universidade Estadual de Campinas, Campinas, São Paulo 13100, Brazil.

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Anomalous Behavior of Surface Acoustic Waves in Cu/Nb Superlattices

A. Kueny, M. Grimsditch, K. Miyano, I. Banerjee, Charles M. Falco, and Ivan K. Schuller
Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 5 October 1981)

Brillouin-scattering measurements show an anomalous dip in the elastic constants of Nb/Cu superlattices for superlattice wavelengths of $\approx 100 \text{ \AA}$. This dip is correlated with changes in the electrical resistivity of the samples giving the first evidence that electronic effects are responsible for phonon softening in these materials.

PACS numbers: 62.20.Dc, 68.25.+j, 78.35.+c

The production of crystallographically coherent layered structures of two different materials has led to the development of a whole new class of materials called superlattices. The components can be either metals or semiconductors and the superlattices are grown by either thermal evaporation or sputtering. These materials have very interesting properties which can be different from those of either of the constituents. The general interest in these new materials has been motivated both by the potential for discovery of new and as yet unknown physical properties, as well as by possible applications in such diverse fields as x-ray and neutron-beam monochromators,

lasers, and microwave electronics. However, since these structures are produced in the form of thin films many conventional techniques (e.g., ultrasonics and neutron scattering) are not readily applicable to their study.

In the present work we have made the first light-scattering measurements of the elastic properties of metallic superlattices. The results show a remarkable anomaly in the velocity of surface acoustic waves as a function of layer thickness in Nb/Cu layered ultrathin coherent structures (LUCS). This anomaly is correlated with changes in the temperature coefficient of resistivity of the material. At the thickness at

which the coefficient of resistivity changes from positive ("metallic") to negative ("nonmetallic") behavior the acoustic velocity shows an anomalous dip. This is interpreted as evidence for phonon softening due to changes in the electronic properties of the superlattice.

In 1978 Sandercock¹ first showed the feasibility of observing thermally excited surface phonons by means of light scattering. Most investigations to date have dealt with the problem of elucidating the interaction mechanism between the light and the phonons as well as an explanation of other broad spectral features which are observed. The tremendous power of the technique is in studying thin films which, because of the small sample volume, are difficult to study by conventional methods. So far it has only been used in a few instances.²⁻⁶

The samples used in the present work⁷ were Nb and Cu LUCS of total thickness approximately 1 μm on sapphire substrates with individual layers varying in thickness from 5 \AA to 1 μm . For all the results presented here, the Nb and Cu layers were of equal thickness with the modulation wavelength Λ being twice an individual layer thickness. The experiments were carried out at room temperature on a five-pass Fabry-Perot interferometer with use of ~ 200 mW of 5145- \AA radiation from a single-moded argon laser. We verified that up to powers of 500 mW no difference was observed in the position of the Brillouin peaks and hence we conclude that local heating does not play a significant role in our experiments. The scattering geometry is described in Fig. 1 of Ref. 1; we kept $\theta_i - \theta_s$ fixed at 38° (θ_i and θ_s incident and scattered angles, respectively) and varied θ_i between 60° and 80° . The incident light

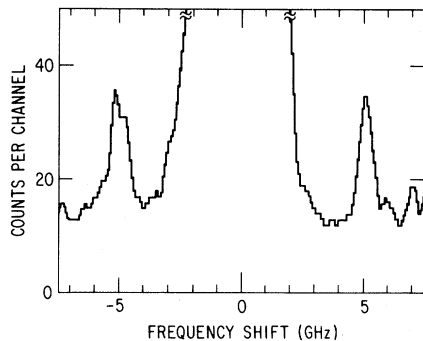


FIG. 1. Brillouin spectrum of a sample with $\Lambda = 20 \text{\AA}$ and $\theta_i = 70^\circ$. The free spectral range is 15 GHz. The time per channel is 0.47 sec and a 9-point smoothing has been performed.

was TM polarized and no analyzer was used in the scattered beam. A spectrum from a sample with good surface quality is shown in Fig. 1. The free spectral range is 15 GHz, $\theta_i = 70^\circ$, and Λ of the sample is 20 \AA . For each sample we measured at least two points on the ω vs \vec{k} dispersion curve in order to obtain the velocity (v_R). The measured velocities are shown in Fig. 2 as a function of the modulation wavelength Λ . For all the results presented here the error bars are estimates based on the number of data points taken for each sample, surface quality, and reproducibility at various points on the surface. Possible systematic errors could cause an overall shift in the ordinate by as much as 5%. The dots and crosses represent two different sets of samples grown 18 months apart.

In order to interpret the results of Fig. 2, the reader is referred to Farnell³ for a review of the properties of surface waves. In the region where $\Lambda \ll \lambda$, where λ is the wavelength of the phonons probed in our experiments ($3000 \text{\AA} < \lambda < 4300 \text{\AA}$), the films can be considered to be homogeneous and to possess cylindrical symmetry around the film normal. In a reference frame with z perpendicular to the film plane, the nonzero components of the elastic moduli tensor are C_{11} , C_{33} , C_{12} , C_{13} , C_{44} , and $C_{66} = \frac{1}{2}(C_{11} - C_{12})$. The velocity of the surface wave is given by⁸

$$v_R = \beta(C_{44}/\rho)^{1/2}, \quad (1)$$

where ρ is the density and β is a function of C_{11} , C_{33} , and C_{13} . Although for materials of symmetry other than isotropic no analytic expression

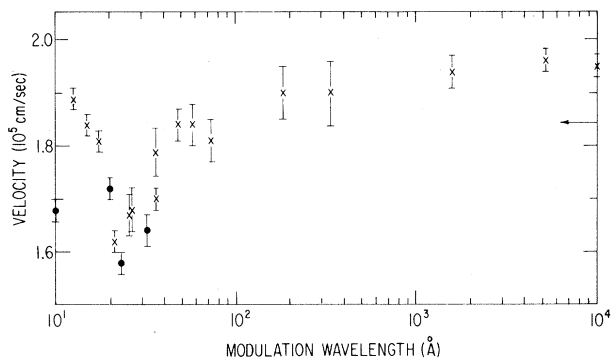


FIG. 2. Surface wave velocity of Nb/Cu superlattices as a function of modulation wavelength. The dots and crosses are values obtained on two series of samples grown 18 months apart. The arrow indicates the expected velocity for films with a modulation $\lesssim 100 \text{\AA}$. The errors in the values of Λ are less than 5%.

exists for β , numerical calculations⁸ for surface phonons in the basal plane of hexagonal crystals performed by us and in Ref. 8 yield $0.86 \leq \beta \leq 0.98$. This insensitivity of β to changes in elastic constants other than C_{44} that cover various orders of magnitude makes us feel that it is very reasonable to assume that the changes in v_R arise mainly from changes in C_{44} .

The problem of the elastic moduli of a structure composed of layers of isotropic materials has been solved by Rytov.⁹ For the particular case of $\Lambda \ll \lambda$, and equal layer thicknesses, we have generalized these results to the case where the individual layers have hexagonal symmetry with their sixfold axes coinciding with the axis of the film. For C_{44} we obtain

$$C_{44}(\text{Nb/Cu}) = \frac{2C_{44}(\text{Cu})C_{44}(\text{Nb})}{C_{44}(\text{Cu}) + C_{44}(\text{Nb})}, \quad (2)$$

where $C_{44}(\text{Cu})$ and $C_{44}(\text{Nb})$ are the elastic constants for Cu and Nb layers, respectively. With use of the fact that the densities of Cu (8.93 g/cm^3) and Nb (8.60 g/cm^3) are similar and under the assumption that the appropriate β 's are not very different, then Eqs. (1) and (2) lead to

$$v_R^2(\text{Nb/Cu}) \simeq \frac{2v_R^2(\text{Cu})v_R^2(\text{Nb})}{v_R^2(\text{Cu}) + v_R^2(\text{Nb})}. \quad (3)$$

It is known that Cu grows along a [111] axis in our films; the average velocity in this plane is⁸ $v_R(\text{Cu}) = 1.75 \times 10^5 \text{ cm/sec}$. The Nb layers grow along [110]; our calculated average velocity for such a film of pure Nb is $v_R(\text{Nb}) = 1.95 \times 10^5 \text{ cm/sec}$. These values and Eq. (3) yield $\bar{v}_R(\text{Nb/Cu}) = 1.84 \times 10^5 \text{ cm/sec}$, which is shown by the arrow on the right-hand side of Fig. 2. According to the theory of Ref. 9 one would expect to observe this velocity in all films for which $\Lambda \ll \lambda$. We expect deviations for $\Lambda \gtrsim 1000 \text{ \AA}$ because in these cases the phonons do not average over many layers so that the upper layer will be dominant in determining the velocity of the surface wave.⁴ For $\Lambda \gtrsim 500 \text{ \AA}$ the constituent of the upper layer could be inferred from the color of the surface. We were only able to obtain spectra in samples which exhibited a typical Nb-like color. For thicknesses $\lesssim 500 \text{ \AA}$ the constituent of the uppermost layer can no longer be determined by visual inspection; consequently we do not know if it is Nb or Cu. However, in this case the surface wave averages over several layers so that the identity of the topmost constituent is unimportant. As can be seen, for Λ in the range $100\text{--}1000 \text{ \AA}$ we find reasonable agreement between experiment and

the calculated $v_R(\text{Nb/Cu})$; for $\Lambda > 1000 \text{ \AA}$, the observed value matches the calculated $v_R(\text{Nb})$. However, between 100 and 12.5 \AA a pronounced dip in v_R is observed which according to Eq. (1), we interpret as a drop of $\sim 35\%$ in C_{44} . We should note that with data on only one sample with $\Lambda < 12 \text{ \AA}$, it is not certain at the present time if the subsequent drop in v_R at $\Lambda = 10 \text{ \AA}$ is a real effect. Some of our preliminary results of Brillouin scattering from Nb/Ti samples also appear to show a decrease of v_R below $\Lambda \simeq 15 \text{ \AA}$.

Previously reported studies of the elastic properties of heterostructures^{10,11} removed from the substrate claimed that the biaxial modulus Y of Cu/Ni and Au/Ni *increases* by a factor of ~ 8 for $\Lambda \simeq 18 \text{ \AA}$. The *decreases* we observe are somewhat surprising in view of these reported increases of Y in similar types of heterostructures. However, we note that in the reference frame used here Y is given by

$$Y = (C_{11} + C_{12}) - 2C_{13}^2/C_{33} \quad (4)$$

and hence no direct contradiction with a decrease in C_{44} is present. In addition, earlier measurements on Cu/Ni heterostructures have failed to observe an enhancement of the elastic constants in samples that were not removed from the substrate.¹² Because of the arguments given previously, we feel that it is unlikely that any changes in C_{ij} , which might lead to an increase of a factor of 8 in Y , could be responsible for changes in β large enough to account for the observed decrease in v_R .

The question that remains now is to explain the observed decrease in C_{44} of the sample and hence, through Eq. (2), the decrease in C_{44} of Cu and/or Nb which is induced by the layering. [Note that C_{44} is defined in the reference frame of the film and *not* in the crystallographic reference frame. As such C_{44} will be an average of the elastic moduli governing the propagation of transverse modes in a (111) plane of Cu or a (110) plane of Nb.] The dip in the elastic constants might arise from either structural changes (such as a sudden decrease in grain size) which would alter the phonon spectrum or changes in the electronic structure of the material at $\Lambda \simeq 21 \text{ \AA}$. Down to $\Lambda \simeq 20 \text{ \AA}$ no unusual behavior is observed in the θ - 2θ x-ray diffraction from our layered materials (we should stress that this kind of x-ray measurements is only sensitive to structure perpendicular to the layers). Below this thickness the x-ray peaks broaden, implying that the material is becoming more disordered. It is therefore

hard to explain both a decrease in v_R and a subsequent increase due to structural changes as Λ is decreased.

A more likely explanation is the electronic contribution to the elastic moduli. One possible mechanism is analogous to that proposed by Keyes¹³ to account for effects due to free carriers in semiconductors. In a nutshell, his argument is as follows: When a phonon modulates the band structure of a material lifting certain degeneracies, it allows a redistribution of the electrons or holes. This redistribution reduces the free energy and thus effectively lowers the elastic constant. Considering that degeneracies in the band structure and a high density of states (which allows substantial rearrangement of the electrons) are most likely to occur at the boundary or at the center of the Brillouin zone, we would expect a large contribution only if the Fermi energy lies close to one of these regions of the Brillouin zone. A very simple argument shows that the Fermi energy will be folded to the zone center when

$$K_F = n 2\pi/d, \quad (5)$$

where K_F is the Fermi wave vector, n an integer, and d the layer thickness. With the value $K_F = 1.36 \text{ \AA}^{-1}$ for Cu, the lowest three solutions for d are 4.6, 9.2, and 13.8 and hence one could expect minima in the elastic constants at $\Lambda = 9.2, 18.4, 27.6, \dots \text{ \AA}$. This is to be compared with the experimentally observed dip at $\Lambda = 21 \text{ \AA}$ and perhaps one at $\sim 10 \text{ \AA}$. At larger values of Λ one would expect the effect to be masked by inhomogeneities in the layer thickness. It is obvious that a complete check of this simple argument is not possible without a full band-structure calculation for the layered structure.

A second explanation can also be proposed by noting that at the thickness at which the elastic constant shows the dip, the temperature coefficient of electrical resistivity (which is roughly independent of temperature between 50 K and room temperature) changes sign.¹⁴ This change in sign is related to progressive localization^{15,16} and Coulomb correlation^{16,17} effects as a function of layer thickness. The opening up of a Coulomb correlation gap at the Fermi energy would be reflected by an anomalous behavior in the elastic constants. This explanation is qualitatively similar to that used to explain anomalous changes in the lattice parameters of binary alloys where energy gaps open up at the Fermi surface as it touches the Brillouin zone.¹⁸

In conclusion, the acoustic velocity of Nb/Cu metallic superlattices shows an anomalous dip as a function of layer thickness. It is suggested that this effect may be due to the removal of degeneracies by the new periodicity imposed by the superlattice or by progressive localization effects as a function of layer thickness. However, irrespective of the possible explanations based on structural or electronic origin, we emphasize the correlation between the transport properties and the elastic constants both of which show anomalies at $\Lambda \cong 20 \text{ \AA}$.

We thank Q. S. Yang for help in preparing some of the samples used in this study. We acknowledge useful conversations with M. Azbel, F. Blatt, R. C. Dynes, and Y. Imry. This work was supported by the U.S. Department of Energy and the U.S. Office of Naval Research under Grant No. N00014-80-F-0074.

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Alloy Clustering in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ Compound Semiconductors Grown by Molecular Beam Epitaxy

P. M. Petroff, A. Y. Cho, F. K. Reinhart, A. C. Gossard, and W. Wiegmann

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 2 October 1981)

Direct evidence of alloy clustering in the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloy system is presented. Clustering is observed *only* on the nonpolar surface of GaAs. An exchange reaction model is proposed to account for the existence of a surface-orientation-dependent miscibility gap for this alloy system.

PACS numbers: 68.20.+t, 68.45.-v, 68.55.+b, 73.40.Lq

Alloy clustering in compound semiconductors has recently been suggested to explain the photoluminescence features of GaAs- $\text{Ga}_{1-x}\text{Al}_x\text{As}$ multi-quantum-well lasers grown by metal-organic vapor deposition.¹ The coexistence of two solid phases with different compositions necessary for defining clustering is very surprising for this alloy system since thermodynamic calculations² do not indicate a miscibility gap. However, computed phase diagrams only deal with thermodynamic properties of the bulk crystal. In the case of solid solutions formed by epitaxy at a vacuum-crystal surface, it might be expected that different thermodynamic equilibria exist for each different crystal surface and that these equilibria will differ with environment. The details of surface thermodynamics are not well enough understood to compute a "surface phase diagram" which takes into account the effects of surface reconstruction, the possibility of exchange reactions, and surface diffusion kinetics. However, crystal growth techniques such as molecular beam epitaxy (MBE)³ offer the possibility of measuring experimentally some features of the surface phase diagram under controlled conditions. In this Letter we report the first evidence of a surface-orientation-dependent phase diagram for the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloy system grown by MBE. A miscibility gap is reported and the structure and composition in the solid solution suggest the existence of a spinodal reaction.

$\text{Ga}_{1-x}\text{Al}_x\text{As}$ ($0.15 \leq x \leq 0.5$) epitaxial layers

have been deposited by MBE^{3,4} at a temperature $T_s = 600^\circ\text{C}$, under growth conditions that would be As stabilized for a (100) growth. The GaAs substrate orientation was (110) for some depositions and for others $\pm 2^\circ$ vicinally oriented from [110] with tilt axis parallel to the $[\bar{1}10]$ direction. These vicinally oriented substrates contain surface steps with ledges parallel to $[\bar{1}10]$ which are terminated either by Ga or As bonds. Typical growth rates are $1 \mu\text{m/h}$. The substrate preparation prior to the MBE deposition consisted of a standard bromine methanol etching and heating in UHV at a temperature of 650°C to remove the remaining oxide. The surface reconstruction of the (110) surface observed by reflection high-energy electron diffraction was (1×1) . It has been established by ultraviolet photospectroscopy⁵ and theoretical calculations⁶ that surface relaxation of the outer layer takes place in such a way that the As moves out by 0.2 \AA and the Ga moves in by 0.45 \AA . The total displacement is 0.65 \AA for atoms on the surface, but it is expected to be more important at the steps for the vicinally oriented (110) surface.

In addition, $\text{Ga}_{1-x}\text{Al}_x\text{As}$ depositions on (100)-oriented GaAs substrates were performed. For these (100)-oriented substrates and films the reconstructed surface was $C(2 \times 8)$. $\text{Ga}_{1-x}\text{Al}_x\text{As}$ films were also deposited on (110) GaAs substrates by liquid-phase epitaxy (LPE)² using the standard graphite crucible process. The growth rate for these films was $\geq 10 \mu\text{m/h}$ and the growth