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Structural Characterization of Cu/Ni Superlattices by X-ray Diffraction Modeling

S. J. Lee, R. Bohmer[1] and W. Abdul-Razzaq[1]

Kyungdong University, Toseongmyun, Bongpori, San 91-1, Kangwondo, Korea
[1]Department of Physics, West Virginia University, Morgantown WV 26506, U.S.A.

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The structure of a series of Cu/Ni is characterized by using a program, SUPREX, to model the x-ray diffraction patterns, multilayers. The samples had nominal layer thickness of 3/3, 7/7, 13.5/13.5, 20/20, 30/30, 50/50, 80/80, 100/100, and 200/200 Angstroms. The diffraction patterns were taken around the (111) peak for the two constituent materials. A kinematical model is used to characterize the diffraction patterns and the parameters for the model are described. An initial model is calculated using initial guesses for the parameters. The model is then fit to the data by reducing χ^2 using the Levenberg-Marquardt algorithm. The samples are shown to be high quality supperlattices.

1. Introduction

Superlattices, which consist of layers (films) of two different materials alternating in a periodic fashion, have been the subject of recent study. The magnetic, transport, mechanical, and superconducting properties of these materials are greatly affected by their additional periodicity [1-5]. It is important to be able to characterize the structure of these materials to understand their physical properties. X-ray diffraction has proven to be an excellent method for studying the structure of superlattices [1, 6-9]. It is nondestructive, gives information on the atomic scale, and is affected by many structural properties including strain and interfacial roughness.

From the experimental X-ray diffraction pattern, which generally exhibits a main peak surrounded by several satellite peaks, the intensity of the peaks, their widths, and their positions can be measured. Using these measurements, the average lattice spacing, the modulation wavelength, and the structural coherence length can be calculated directly. Eric Fullerton *et al.* [4] have developed a program called SUPREX (SUPerlattice Refinement from X-rays) to model the measured X-ray spectra using different formalisms and to fit the calculated spectra to the measured spectra using a χ^2 fitting procedure. In this study we characterized the periodic structure of our Cu/Ni samples by using the SUPREX program.

2. Experimental

The Cu/Ni samples used in this study were prepared by means of a UHV sputtering unit. The system was pumped down to a base pressure of $\sim 3 \times 10^{-9}$ Torr before admitting ultrahigh-purity Ar gas to the chamber. The Ar gas was passed through a cold trap at 100 K and then through a gas purifier to remove impurities such as O_2 and N_2 by reaction with a hot Ti based alloy. A computer controlled substrate holder plate moved the substrate quickly between the Cu and Ni sources. The samples were grown on the (111) planes of silicon single crystal for both materials.

The Cu/Ni samples were prepared with the nominal thickness of layers of each material equal. For each sample, the number of bilayers was adjusted so that the total nominal thickness of each sample was 5000 Å. The nominal thickness, t_A/t_B, for these samples in are: 3/3, 7/7, 13.5/13.5, 20/20, 30/30, 50/50, 80/80, 100/100, and 200/200. The samples were X-rayed using the Rigaku D/Max-B System at West Virginia University.

3. Results and Discussion

The resulting spectra are shown in Fig. 1 through 3 (dotted lines). The samples with the smallest layer thickness, 3/3 and 7/7, demonstrate a main peak only. Satellite peaks begin to appear in the 13.5/13.5 sample and become more pronounced with increasing layer thickness. With the 50/50 sample, secondary satellites begin to appear. By the 100/100 sample, the satellite peaks begin to dominate and by the 200/200 sample the main peak is almost totally suppressed. The two satellite peaks for the 200/200 sample are approaching the position of peaks for bulk samples of the two materials.

The solid lines in Fig. 1 through 3 were calculated for ideal superlattices using the kinematical model in the SUPREX program. These ideal models were calculated by setting the lattice spacings between atomic layers (d's)

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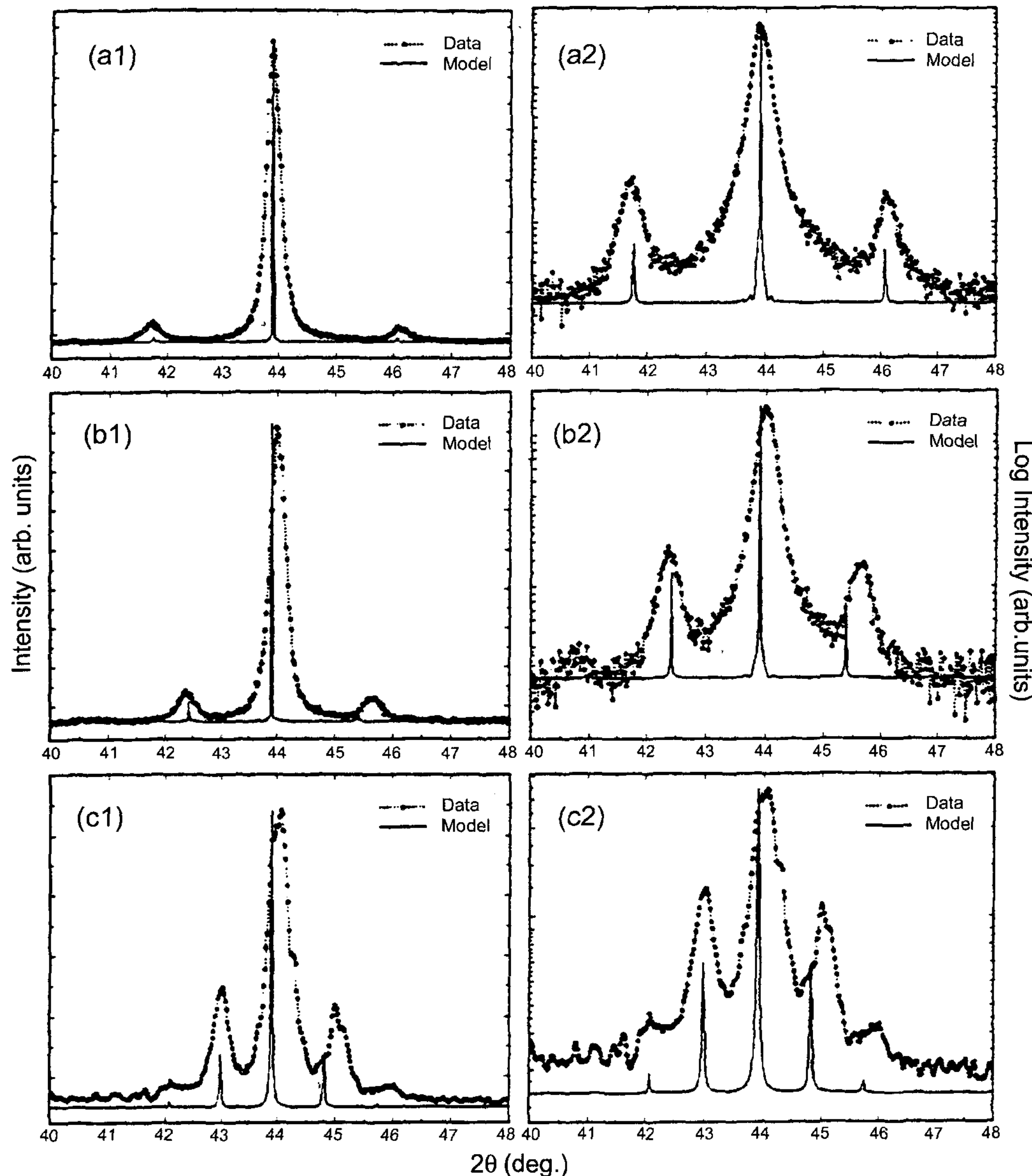

Fig. 1. Experimental (dotted line) and ideal model (solid line) X-ray diffraction patterns for Cu/Ni samples with layer thicknesses of: (a) 3/3 (b) 7/7 and (c) 13.5/13.5. The left column is linear scale and right column is log scale.

equal to those for (111) planes in the bulk material; 2.088 Å for Cu and 2.034 Å for Ni, which were calculated using the equation: $d^2 = a^2 / (h^2 + k^2 + l^2)$ where a is the lattice parameter for cubic lattices and h, k, l are the indices of planes. The value of a is 3.61 Å for Cu and 3.52 Å for Ni. The distance between layers of Cu and Ni was set equal to the average of the d's. The average number of atomic planes in each layer was chosen such that the layer thicknesses were equal to the nominal ones. The statistical widths and the lattice strain parameters were set to zero. The scaling factor and background intensity were set to a convenient value to make the graphs comparable. The characteristics listed above for the experimental spectra are also exhibited by the ideal models.

The 30/30 sample was chosen to be fit first, because it is in the middle of the list of samples ordered by layer thickness and exhibits distinct satellites as well as a distinct main peak. The process for fitting the model to the data was studied using this sample. According to Fullerton, it is useful to know the influence of the parameters on the diffraction profile and χ^2. Due to the complexity of equations used in the fitting, local minima will often prevent the algorithm from converging to the absolute minimum. Therefore, it is important to chose the starting parameters for the fitting to avoid local minima. Starting from the ideal model for the 30/30 sample, each parameter was varied individually for four fitting iterations and the changes in the characteristics of the diffraction spectra were measured.

The results are shown in Table 1. For each parameter, the change in that parameter, the amount χ^2 was reduced, and change in the properties of the three peaks are shown. The χ^2's between the ideal model and the data and between the

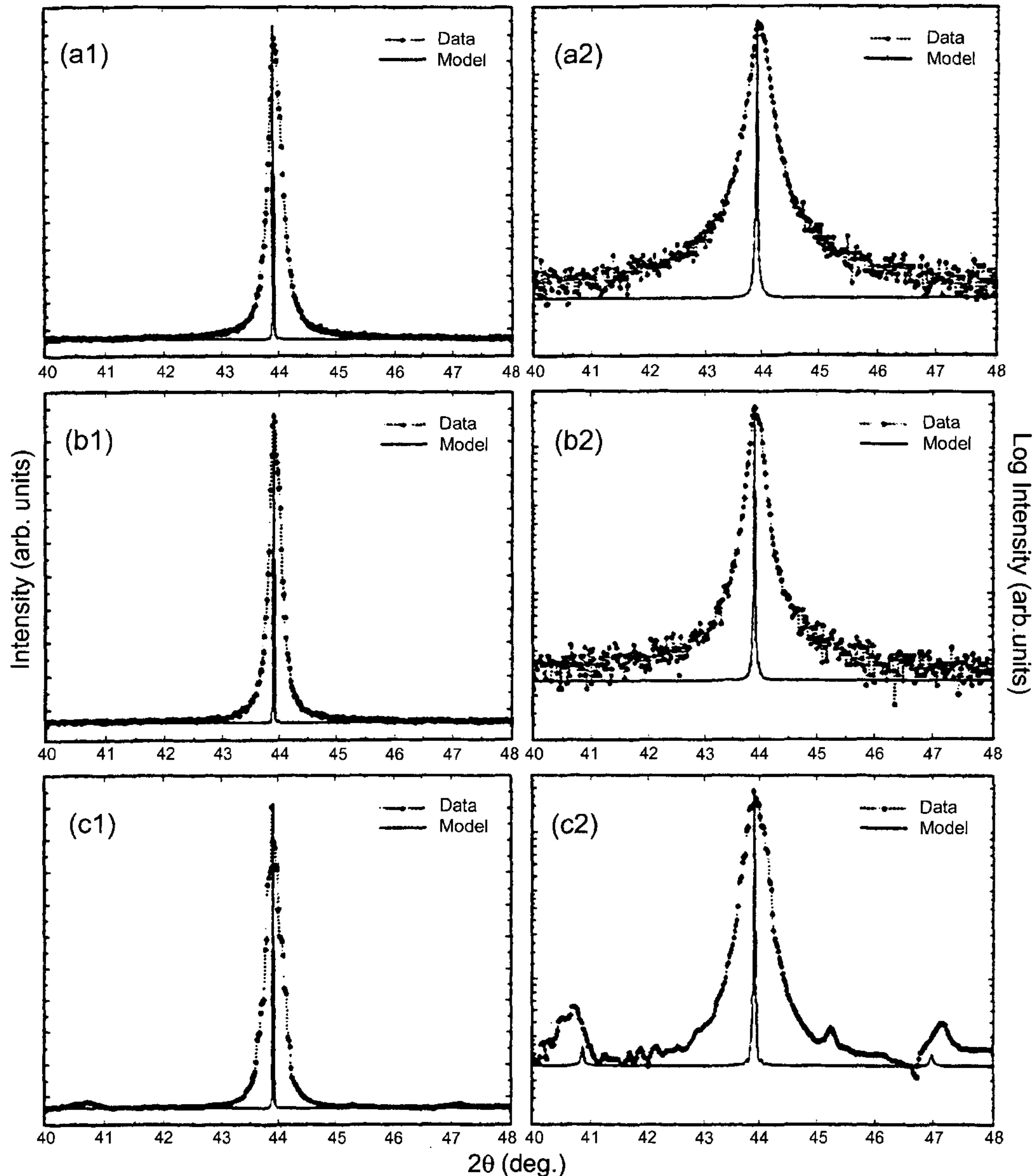

Fig. 2. Experimental (dotted line) and ideal model (solid line) X-ray diffraction patterns for Cu/Ni samples with layer thicknesses of: (a) 20/20 (b) 30/30 and (c) 50/50. The left column is linear scale and right column is log scale.

model after four iterations and the data were calculated and the difference between these two values was recorded. For each peak, the changes in the position, intensity, and width (FWHM) were recorded. The parameters that led to the greatest reduction in χ^2 were Gaussian distribution widths for d (σ_d's) and Gaussian distribution width for d,int ($\sigma_{d,int}$); d,int is distance between layers of material A (Cu: copper) and material B (Ni: nickel). These parameters were also the ones that had the largest increases in the width which, from looking at Fig. 3(b), is the characteristic that shows the greatest difference between the ideal model and the data. One of these parameters should be fit first to avoid problems with finding local minima. $\sigma_{d,int}$ was chosen to fit first because the value of d,int was set to the average of the d's for the two materials and was not based on any prior knowledge of the supperlattice structure. When two or more parameters are closely related and only one is being fit, the fit parameter may adjust to accommodate for the error in the other value(s). This means that more than one parameter should be fit at a time. However, fitting too many parameters at once can cause problems due to the possibility of degeneracy in the reduction of χ^2. Since d,int is closely related to $\sigma_{d,int}$, these two parameters were fit together.

The scaling factor and background intensity were allowed to vary throughout the fitting procedure to keep the other parameters from compensating for any errors in these values; most of the parameters caused a reduction in the intensity, and the scaling factor had initially just been set to a convenient value. After fitting d,int and $\sigma_{d,int}$ reached a minimum, the d's and σ_d's were fit followed by the average numbers of atomic planes in layer (n's) and Gaussian distribution widths for n (σ_n's) . The deviations of lattice con-

Table 1. Results of χ^2 fitting each parameter individually for four iterations. The amounts that the fitting parameter changed and the amounts that χ^2 was reduced are shown. The change in the characteristics (p=position, i=intensity, w=width) of the three peaks are also shown. Intensity is in arbitrary units. The position is that of the maximum intensity of the peak measured in 2θ degrees. Width is FWHM measured in $10^{-3} \times 2\theta$ degrees

Param.	ΔParam.	$\Delta\chi^2$		low peak	main peak	high peak
d_{int}	−0.0055	−85,187	p:	+0.02	+0.01	+0.02
			i:	−1.64	+119.17	+3.31
			w:	+1.66	−1.42	−8.74
d[A]	−0.001	−102,104.25	p:	+0.02	+0.01	+0.02
			i:	−1.98	+118.71	+1.04
			w:	+1.66	−1.42	+0.01
d[B]	−0.0008	−87,725.75	p:	+0.02	+0.01	+0.02
			i:	+3.62	+109.58	+6.15
			w:	+1.67	−2.14	+1.26
n[A]	−0.4831	−117,194.25	p:	−0.01	+0.01	+0.04
			i:	−14.58	+50.42	−7.91
			w:	+5.83	−0.71	+4.38
n[B]	+0.3825	−79,588.25	p:	+0.04	+0.01	−0.01
			i:	−12.23	+142.05	+7.25
			w:	+7.5	−2.14	−1.24
Δd_1[A]	−0.0081	−119,653.5	p:	+0.02	+0.01	+0.02
			i:	+2.09	+93.36	+4.05
			w:	+0.83	−1.42	−0.62
Δd_1[B]	−0.0078	−111,215.5	p:	+0.02	+0.01	+0.02
			i:	+5.43	+91.02	+7.22
			w:	+0.83	−2.85	−0.62
Δd_2[A]	−0.0081	−120,079.25	p:	+0.02	+0.01	+0.02
			i:	+2.09	+93.23	+4.06
			w:	+1.66	−0.72	−0.62
Δd_2[B]	−0.0078	−110,817	p:	+0.02	+0.01	+0.02
			i:	+5.43	+93.13	+7.22
			w:	+0.83	−1.42	−0.62
σ_d[A]	+0.0648	−724,751.75	p:	0	0	0
			i:	−86.79	−1028.79	−61.52
			w:	+124.17	+125.71	+165.0
σ_d[B]	−0.0619	−649,895.75	p:	+0.02	0	+0.02
			i:	−85.05	−1023.52	−62.59
			w:	+131.66	+125.01	+141.25
σ_n[A]	+13.804	−499,057.63	p:	−0.22	+0.16	+0.21
			i:	−112.92	−986.41	−86.16
			w:	+174.17	+80.71	0
σ_n[B]	+1.6833	−72,211.75	p:	0	0	0
			i:	−63.49	−96.37	−12.31
			w:	+55.0	+3.57	+10.0
$\sigma_{d,int}$	+0.2008	−692,963	p:	0	0	0
			i:	−86.83	−1038.84	−62.93
			w:	+130.83	+127.86	+156.26
initial values		2,445,556	p:	42.42	43.92	45.40
			i:	150.39	1502.92	116.1
			w:	51.67	57.14	59.37

stant (Δd's) were fit last, then the cycle was repeated until the values of all the parameters stopped changing.

Figure 4 through 7 show the calculated spectra and the data after each step of the fitting cycle described above. Fig. 6(a) shows the result after fitting d,int and $\sigma_{d,int}$. These values changed to: d,int=1.9882 Å and $\sigma_{d,int}$=0.1982 Å. The result of fitting the d's is shown in Fig. 4(b). The d for Cu changed from 2.088 Å to 2.0953 Å and the d for Ni changed from 2.034 Å to 2.027 Å. The parameter, σ_d for Cu became 0.0135 Å and for Ni, 0.0028 Å (Fig. 5(a)). N for Cu changed from 15.3678 to 14.5051 and for Ni from 15.7493 to 14.5890. The values for the strain factors became: Δd_1[A]=0.0710, Δd_1[B]= −0.0710, Δd_2[A]=0.0310, and Δd_2[B]= −0.0312, where Δd_1 and Δd_2 are the deviations

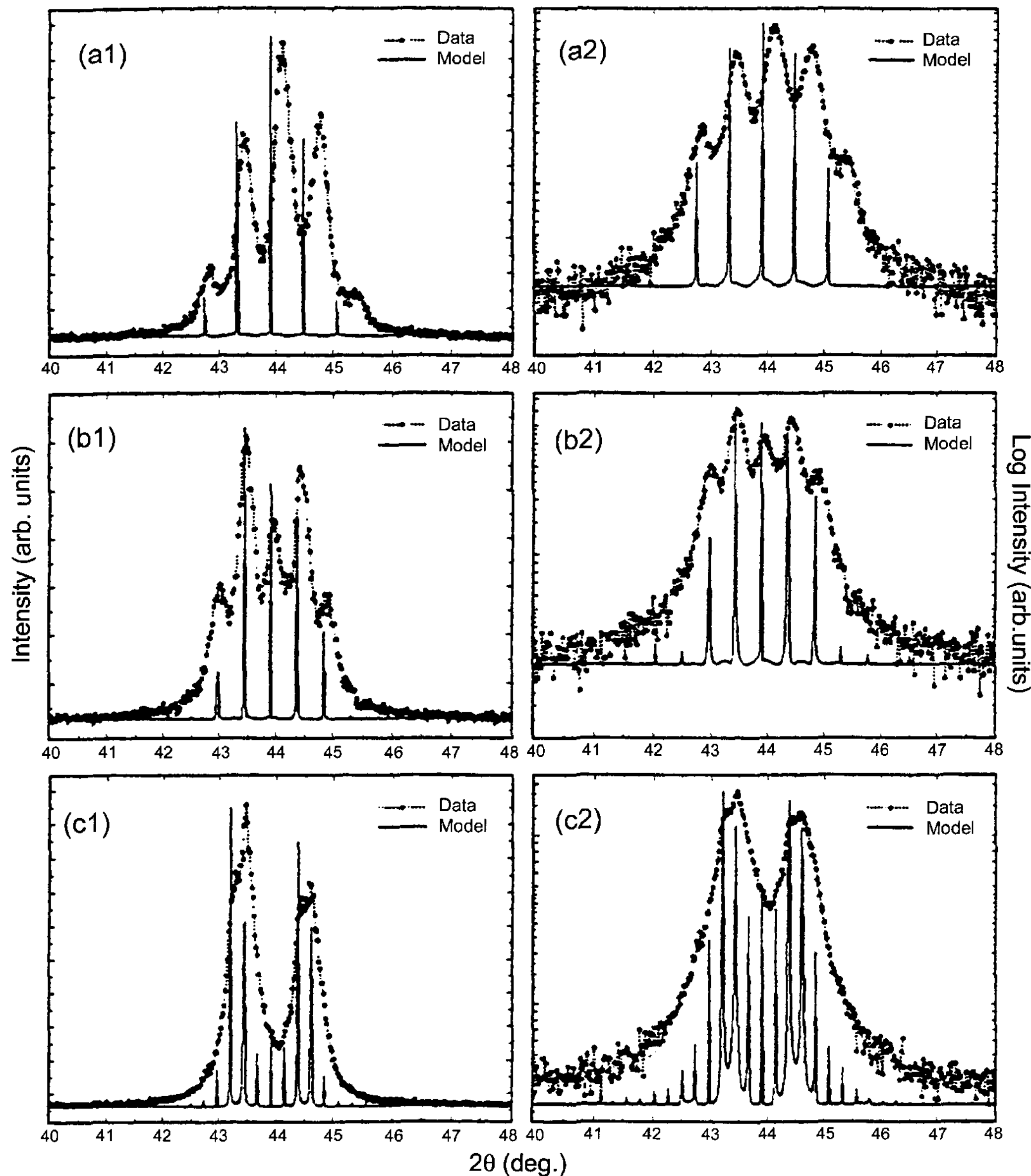

Fig. 3. Experimental (dotted line) and ideal model (solid line) X-ray diffraction patterns for Cu/Ni samples with layer thicknesses of: (a) 80/80 (b) 100/100 and (c) 200/200. The left column is linear scale and right column is log scale.

of lattice constants near the top and bottom of the layer, respectively. This cycle was repeated two more times until the values stopped changing. The result is shown in Fig. 7. The final values of the parameters are shown in Table 2. This process was repeated for the remaining samples. The results are shown in Fig. 8 through 11. Fig. 9, which shows the results for the 13.5/13.5 and 20/20 samples, graphs the log of intensity instead of intensity vs. 2θ because these samples exhibit very small satellite peaks as compared to the main peak. Table 2 contains all the final parameter values for the nine samples used in this study. Since the program stores the values to a greater precision than it will display them, any zero value in this Table can only be assumed to be less than 5×10^{-5}. The values in Table 2 exhibit many of the expected characteristics. The d's for the thickest samples are very close to the values for bulk material while their strain factors are relatively large. The d's for the thinnest samples vary more from the bulk values but the strain factors are relatively small. This is expected because thicker layers should behave like bulk material and only be affected by the other material near the interface while thinner layers will expand or contract across the entire layer. Since Cu has the larger unstrained lattice constant, the lattice mismatch with Ni causes a compressive distortion in the growth plane. This results in a tensile distortion along the growth direction. An increase in d along the (111) direction (growth direction) would be predicted for Cu. The opposite effect would be predicted for the Ni layers. The values of d for each material in Table 2 show a general trend that is consistent with predictions. The fitting gave values for Cu that were larger than the bulk value of 2.088 due to tensile strain and values for Ni are smaller than

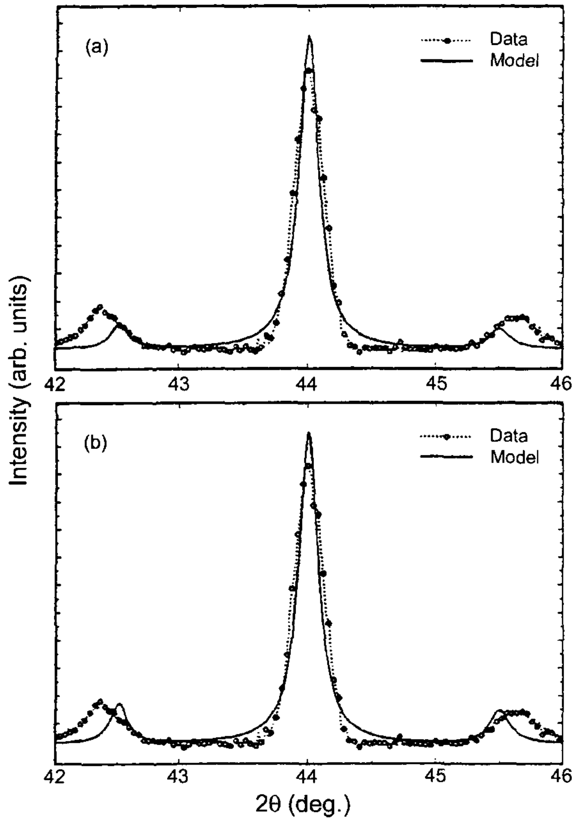

Fig. 4. Results of fitting 30/30 data with the parameters: (a) d,int and $\sigma_{d,int}$, and (b) d [material A] and d [material B].

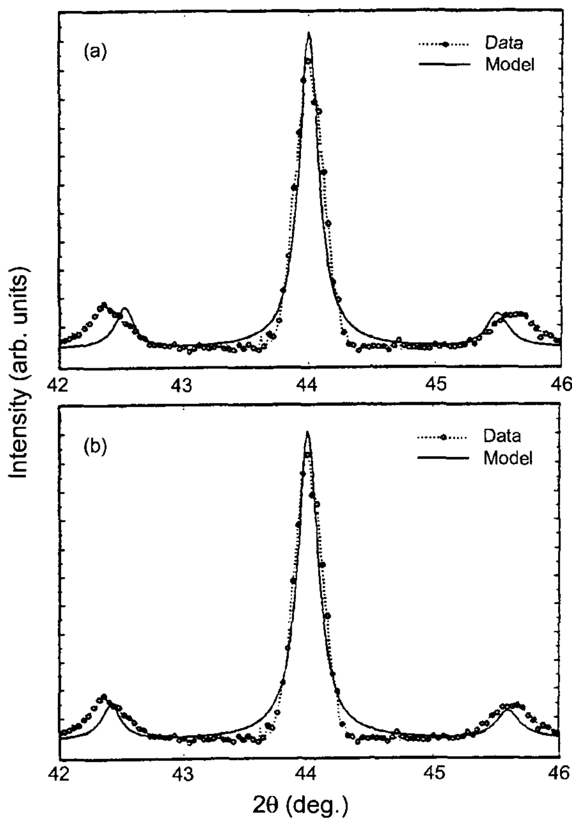

Fig. 5. Results of fitting 30/30 data with the parameters: (a) σ_d for both materials, and (b) n for both materials.

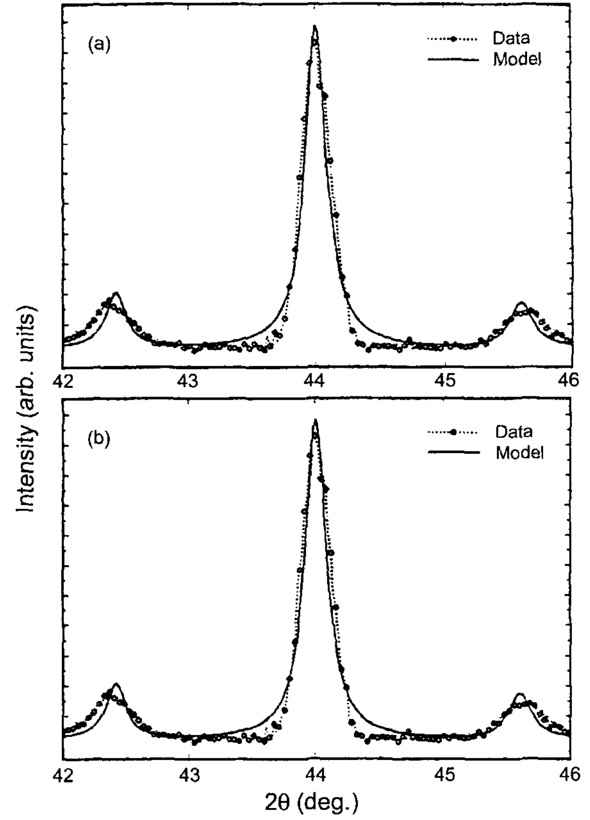

Fig. 6. Results of fitting 30/30 data with the parameters: (a) Δd_1 for both materials, and (b) Δd_2 for both materials.

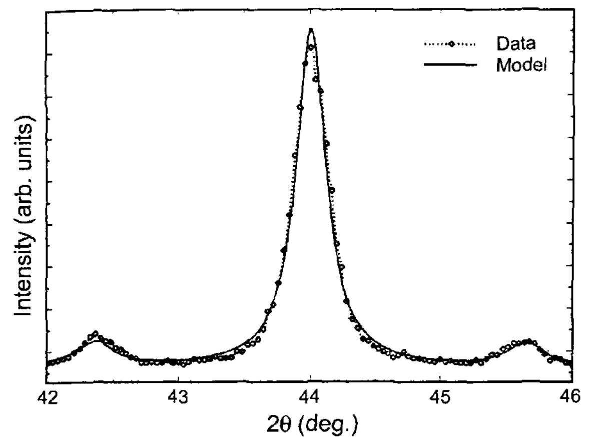

Fig. 7. Results of fitting 30/30 data after three cycles through the fitting parameters.

2.034 due to compressive strain.

The magnitude for d,int is close to the numeric average of Cu and Ni bulk lattice constants for the two thinnest layers and decreases for the thicker layers due to lattice relaxation at the interface. The results from the fitting are consistent with the experimental observation of no satellite peaks in the two thinnest samples. The variation for d is an order of magnitude smaller and also appears to follow a general trend of increasing with increasing layer thickness. This is expected due to the increasing distance between interfaces

Table 2. Final parameter values after complete χ^2 fitting (dens=density of element, f=number of protons in nucleus, # bilay=number of bilayers in superlattice, normal=scaling factor multiplying intensity, bacgr=constant background intensity, modlen (Å)=modulation wavelength)

Parameter	3/3	7/7	13.5/13.5	20/20	30/30	50/50	80/80	100/100	200/200
				Material A: Cu, dens=8.45 ($10^{22}/cm^3$), f=29					
d(Å)	2.0941	2.0662	2.0891	2.0950	2.0931	2.0903	2.0886	2.0865	2.0836
σ_d(Å)	0.005	0.005	−0.0000	−0.0000	0.0301	0.0137	0.0000	0.0305	0.0508
n	2.3763	4.3149	7.4664	10.4996	13.6286	23.7457	34.8157	46.3707	95.8652
σ_n	0.000	0.0829	−0.0001	0.0000	0.8720	0.0000	0.0000	1.2518	0.0000
Δd_1(Å)	0.0137	0.0000	0.0000	0.0001	0.0087	0.0653	−0.1415	−0.1789	0.0312
Δd_2(Å)	−0.0006	−0.0004	0.0000	−0.0005	−0.0016	−0.0705	−0.0012	−0.0115	−0.0048
thickness	2.9072	6.8486	13.5090	19.9011	26.4468	47.5365	70.3548	94.3003	197.7157
				Material B: Ni, dens=9.14 ($10^{22}/cm^3$), f=28					
d(Å)	2.0313	2.0552	2.0329	2.0272	2.0291	2.0314	2.0346	2.0344	2.0326
σ_d(Å)	0.0023	0.0036	−0.0000	−0.0000	0.0231	−0.0003	−0.0000	0.0393	0.0573
n	2.5819	4.4042	7.6391	10.7642	14.4252	23.9962	37.6381	47.7648	99.1170
σ_n	0.0000	0.2919	−0.0000	0.0000	2.0246	0.0000	0.0000	0.9466	0.0000
Δd_1(Å)	−0.0125	0.0000	0.0000	−0.0002	−0.0079	0.1351	0.1323	0.1915	0.1450
Δd_2(Å)	−0.0015	0.0004	0.0000	0.0005	0.0017	−0.1253	0.5500	0.0099	0.0528
thickness	3.1866	6.9971	13.4969	19.7946	27.2292	46.7343	74.8060	95.5229	199.8104
				multilayer					
d_{int}(Å)	2.0562	2.0564	2.0586	2.0594	2.0021	1.9183	2.0335	1.9552	1.9938
$\sigma_{d,int}$(Å)	0.0971	0.1189	−0.1768	0.1984	0.2090	0.3659	0.4351	0.4596	0.5577
# bilay	833	357	185	125	83	50	31	25	12
normal	0.0005	0.0004	0.0013	0.0010	0.0007	0.0001	0.0009	0.0002	0.0016
bacgr	28.8054	32.3605	17.6111	25.8683	23.2264	28.6350	23.0595	30.9802	47.9295
modlen(Å)	10.2062	17.9585	31.1230	43.8145	57.6802	98.1074	149.2278	193.7736	401.5138

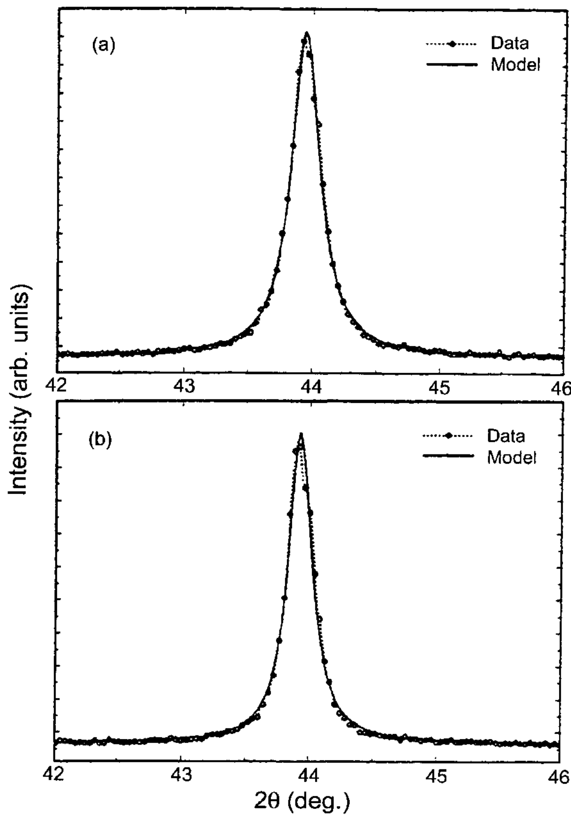

Fig. 8. Final fitting results for (a) the 3/3 sample and (b) the 7/7 sample.

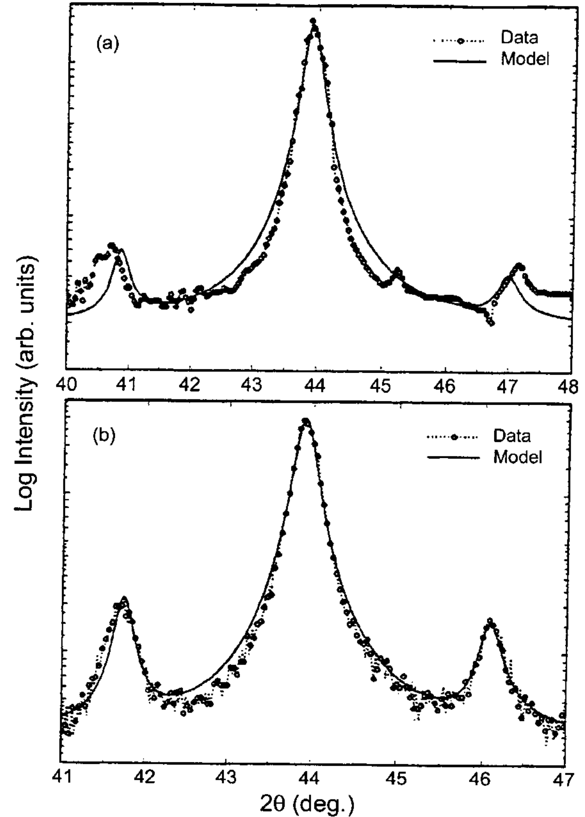

Fig. 9. Final fitting results for (a) the 13/13 sample and (b) the 20/20 sample.

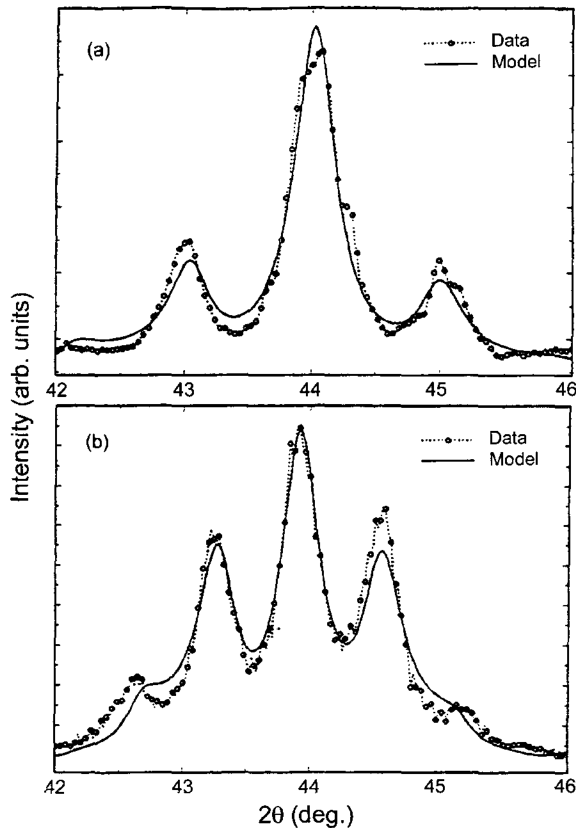

Fig. 10. Final fitting results for (a) the 50/50 sample and (b) the 80/80 sample.

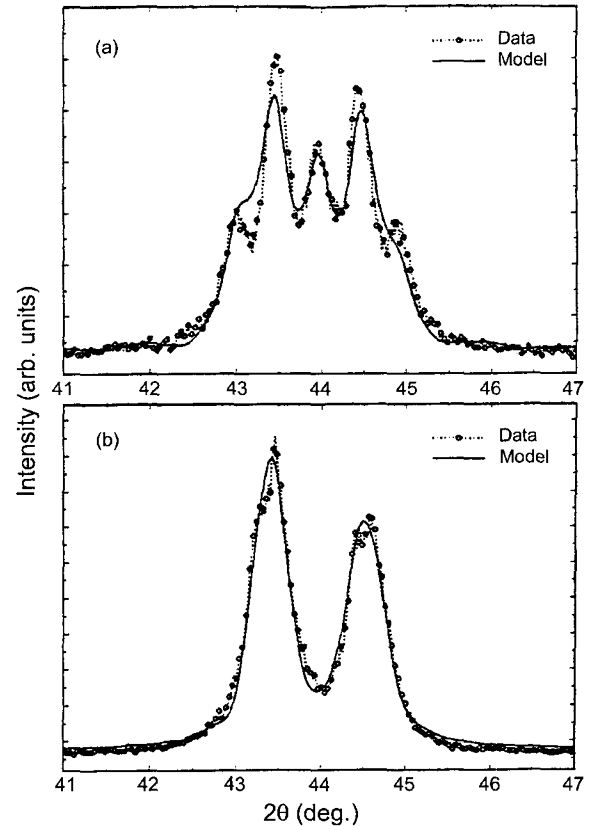

Fig. 11. Final fitting results for (a) the 100/100 sample and (b) the 200/200 sample.

and the increasing strain values making the interfaces more independent of each other. The parameters are also consistent with the growth conditions. The layer thicknesses were expected to be equal. The differences in layer thicknesses are less than 10% for all the samples and less than 2% for most. Also, the variation in the number of monolayers is less than 5% of the actual number.

4. Conclusions

In this study, the SUPREX program was successfully implemented as a diagnostic tool for the determination of the structure of metallic superlattices. It can be used as an integral part of any study of the properties of superlattices. Many of the physical properties of these systems are sensitive to structural properties, making the determination of the structure a necessary part of the interpretation of studies on these systems.

From this study, it was concluded that the samples used were of high quality. The value for the variation in d for both layers was very small for all the samples, showing that all the interlayer separations are very close to average values. Also the value of d,int is of the order of d for each material indicating a localized interface.

Acknowledgement

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References

[1] "Physics, Fabrication and Application of Multilayered Structures" edited by P. Dhez and C. Weisbuch (Plenum Press, New York, 1988).

[2] S. F. Cheng, A. N. Mansour, J. P. Teter, K. B. Hathaway, and L. T. Kabacoff, Phys. Rev., B **47**, 206 (1993).

[3] B. G. Almeida, M. A. Salgueiro, J. B. Sousa, and N. K. Flevaries, J. Mag. and Mag. Mat., **121**, 443 (1993).

[4] E. E. Fullerton, D. M. Kelly, J. Guimpel, and I. K. Schuller, Phys. Rev. Lett., **68**, 859 (1992).

[5] B. Vidal and P. Vincent, Appl. Optics **23**, 1794 (1984).

[6] I. K. Schuller, Phys. Rev. Lett., **44**, 1597 (1980).

[7] L. S. Palatnik, A. A. Koz`ma, I. F. Mikhailov, and V. N. Maslov, Sov. Phys. Cryst., **23**, 316 (1978).

[8] Y. P. Khapachev and G. F. Kuznetsov, Sov. Phys. Cryst., **28**, 12 (1983).

[9] J. H. Underwood and T. W. Barbee, Jr. App. Optics **20**, 3027 (1981).