Materials Science and Engineering, A126 (1990) 19-24

Structural and Elastic Property Changes in Ag/Co Superlattices Induced by High Energy Ion Irradiation

ERIC FULLERTON and IVAN K. SCHULLER

Department of Physics, B-019, University of California, San Diego, La Jolla, CA 92093 (U.S.A.)

R. BHADRA and MARCOS GRIMSDITCH

Argonne National Laboratory, Argonne, IL 60439 (U.S.A.)

STEVEN M. HUES

Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5000 (U.S.A.)

(Received April 21, 1989)

Abstract

The shear elastic modulus and structural properties of a series of Ag/Co superlattice films have been characterized using Brillouin scattering and X-ray diffraction. A softening of the shear modulus of the unirradiated Ag/Co superlattices with decreasing modulation wavelength is observed and is correlated with an expansion in the average lattice spacing. With increasing irradiation fluence, a reduction in the anomalous shear modulus softening and lattice expansion are observed. These reductions imply that the anomalous elastic properties are related to lattice strains present, which are relieved by the irradiation.

1. Introduction

Metallic superlattice films have been shown to exhibit anomalous elastic properties as a function of modulation wavelength (the thickness of one A/B layer in an alternating A/B/A/B/A... structure is denoted Λ). The sense of these anomalies is system specific. As a general trend, miscible systems harden as the modulation wavelength is decreased, while immiscible systems soften (for a review see ref. 1).

The elastic properties of layered systems have been a subject of study since 1937 [2]. This initial work and many generalizations which followed (for a list of previous calculations see references in ref. 3) show that the effective elastic constants of a composite system may be taken as averages of the moduli of the constituent materials. In 1970 an article was published [4] in which it was suggested that layered systems containing dislocations could be stronger than the constituent materials. Later experimental studies [5-7] claimed this to be true and the phenomenon was designated as the "supermodulus" effect [6]. For instance, the Cu/Ni system hardens as the modulation wavelength is decreased. On the assumption that the hardening and softening effects may have related causes, the term supermodulus effect has been applied to any wavelength-dependent elastic anomaly.

The underlying mechanism for this effect is a subject of considerable debate in the literature. Because the elastic constants c_{ij} of the layered materials are sometimes greater than expected, even for dislocation-free systems, the original ideas of ref. 4 have not been pursued. The theories that have been subsequently proposed to explain this effect invoked either structural [8-14] or electronic [15-19] changes present in the superlattices. To date, no definitive answer has emerged and, because other experimental tools may shed additional light on this problem, we have embarked on a study of the relationship between high energy ion irradiation and the supermodulus effect.

At high (*i.e.* megaelectronvolt) ion energies, the kinetic energy of the primary ion is transferred to target atoms through electronic and nuclear collision stopping mechanisms (for a review see ref. 20). While a low probability event, at these energies the effect of the nuclear collisions is the production of a uniform concentration of point defects throughout the superlattice film [21].

0921-5093/90/$3.50

These defects (*e.g.* interstitial–defect pairs), usually having a high room temperature mobility, will migrate through the host material until they anneal out at external or internal surfaces (*e.g.* a strained interface) or through direct recombination. Electronic stopping, while a significant source of irradiation damage in dielectric materials, does not contribute to the defect concentration.

The effect of particle irradiation on the elastic moduli of materials has been previously studied for a variety of metals [22, 23] and inorganic salts [24]. In all cases, the particle irradiation has acted to reduce the elastic moduli of these bulk materials. Because of this, the supermodulus effect in a superlattice system such as Cu/Ni, whose biaxial modulus hardens upon decreasing the modulation wavelength, should also be attenuated and the interpretation would be unclear. Therefore the Ag/Co system, whose shear modulus softens with decreasing modulation wavelength [25], was chosen for this study. Preliminary results of this study on a different sample set were obtained and previously reported [26].

If the supermodulus effect is predominantly a result of a strain-related mechanism, then the irradiation-produced defects migrating to the strained internal interfaces will act to relieve this strain and cause a corresponding reduction in the supermodulus effect. In this work, we have studied the effect of high energy ion irradiation on the shear elastic modulus of Ag/Co superlattices using Brillouin scattering and X-ray diffraction.

2. Experimental details

Ag/Co superlattices (about 1 μm thick) were prepared using magnetron sputtering, with a temperature-stabilized computer-controlled sample holder described earlier [27]. The argon sputtering gas pressure was controlled using a residual gas analyzer in feedback mode to assure proper rate control. Structural studies were performed using a computer-controlled Rigaku D-Max II X-ray diffractometer using Cu Kα radiation. Shear elastic constants were measured using Brillouin scattering with a 5 + 2 tandem Fabry–Pérot spectrometer and have a relative error of 1%–2%. The samples are sufficiently thick that no corrections are necessary for the presence of the substrates.

Ion irradiation was performed using a National Electronics Corporation 950H Pelletron. The samples were irradiated with 6 MeV Si^+ ions with doses of 10^{13}, 10^{14}, 10^{15}, 10^{16} and 10^{17} ions cm^{-2}. The 3.5 and 5.3 nm modulation wavelength samples were also irradiated to doses of 6×10^{14} ion cm^{-2}. Computer simulation of the primary-ion range, using the *TRIM 86* code [28], has shown that at this energy the implanted Si^+ ions penetrate more than 1 μm into the sample. Therefore the effects of stress resulting from primary-ion accommodation into the superlattice structure are not important. During irradiation, one half of each film was masked with a metal foil. This unirradiated side was then used as a control, to account for possible instrumental drifts or changes in the samples as a function of time.

3. Results and discussion

Figure 1 shows the acoustic phonon velocities of the unirradiated Ag/Co superlattices, as a function of modulation wavelength. The surface shear elastic constant C_{44} is related to the phonon velocity by the relationship [29]

$$\text{velocity} = \beta \left(\frac{C_{44}}{\rho_m} \right)^{1/2}$$

where ρ_m is the mass density of the film and β (≈ 0.9–1.0) is essentially constant and only weakly dependent upon C_{11}, C_{33}, and C_{13}. The phonon velocity decreases with modulation wavelength (11% from 20 to 3.5 nm) below the calculated value which assumes the bulk shear elastic modulus for each component (broken line in Fig. 1).

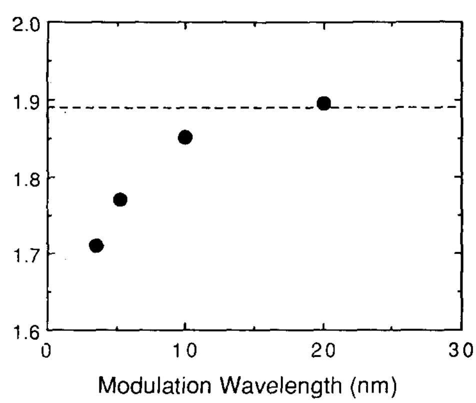

Fig. 1. Acoustic phonon velocities of the unirradiated superlattices as a function of modulation wavelength.

Figure 2 shows the change in phonon velocity of each sample, as a function of irradiation dose. For each modulation wavelength, the material hardens with irradiation dose. It should be stressed that this behavior is opposite to that of pure metals or single crystals and does not reflect a normal radiation damage effect. At a dose of 10^{17} atoms cm^{-2}, Brillouin scattering could not be performed for the 20.0 and 3.5 nm wavelength sample set, owing to poor film surface quality.

Each of the phonon velocity *vs.* irradiation dose plots show a general shape with an initial "floor" value, corresponding to the unirradiated value. At a wavelength-dependent critical dose, the phonon velocity increases to a "ceiling" value which is approximately the same for all wavelengths. The critical dose increases with increasing modulation wavelength as shown in Fig. 3. The significance of this dependence is not fully understood at this time. A similar variation in interdiffusion coefficients as a function of modulation wavelength, induced by thermal annealing, has also been noted by Henein and Hillard [30]. The mobility of the defects introduced into the superlattice by the ion irradiation may be affected by the periodicity in an analogous manner. However, without further study, any conclusions are speculative.

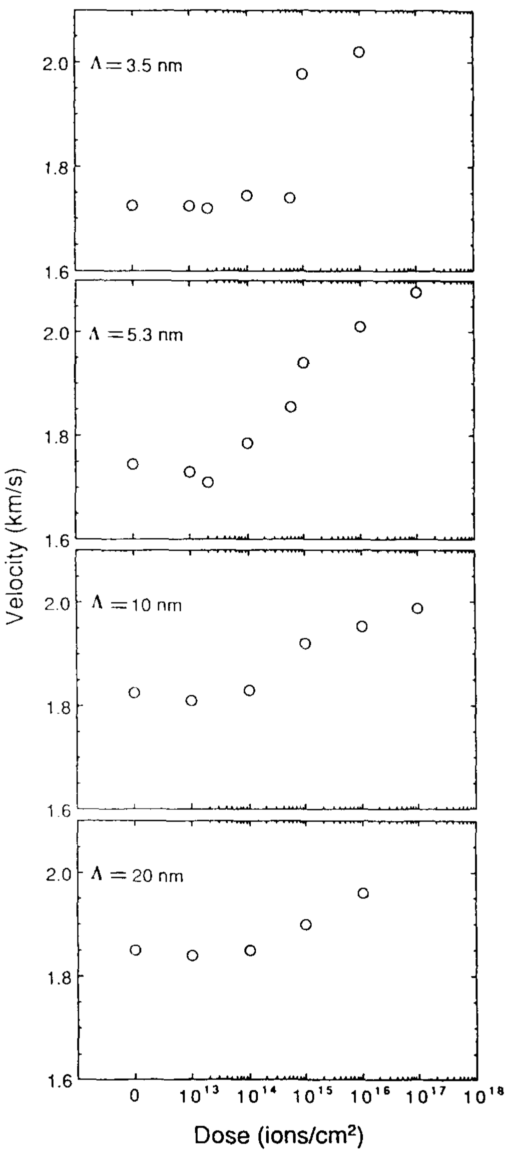

Fig. 2. Acoustic phonon velocities of the superlattice samples as a function of irradiation dose with 6 MeV Si^{+} ions.

The structural properties of the samples were studied by X-ray diffraction. Both θ–2θ scans and θ scans (rocking curves) were performed on the samples before and after irradiation. θ–2θ X-ray spectra, prior to irradiation, are shown in Fig. 4. For $\Lambda = 10.0$, 5.3 and 3.5 nm samples, well-resolved satellite peaks are observed, indicating a layered structure with a normal coherence length greater than Λ. The $\Lambda = 20$ nm spectra have Ag(111) and Co(002) peaks which are broadened by unresolved satellite peaks; in addition to the main peaks, poorly resolved satellite peaks may also be observed between the main peaks. The average lattice parameter $\bar{d}$ normal to the layers determined from the central peak position increases with decreasing modulation [31]. The correlation between the expansion in $\bar{d}$ and the decrease in the phonon velocity has been observed in a number of immiscible systems, such as Nb/Cu [32, 33], Mo/Ni [34] and Mo/Ta [35].

The $\Lambda = 3.5$ and 5.3 nm samples exhibit similar structural effects as a function of irradiation.

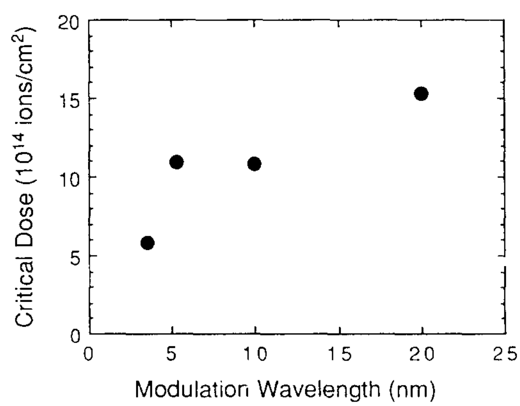

Fig. 3. Plot of the irradiation dose required to attain the inflection point in the phonon velocity *vs.* irradiation dose plot ("critical dose") *vs.* modulation wavelength.

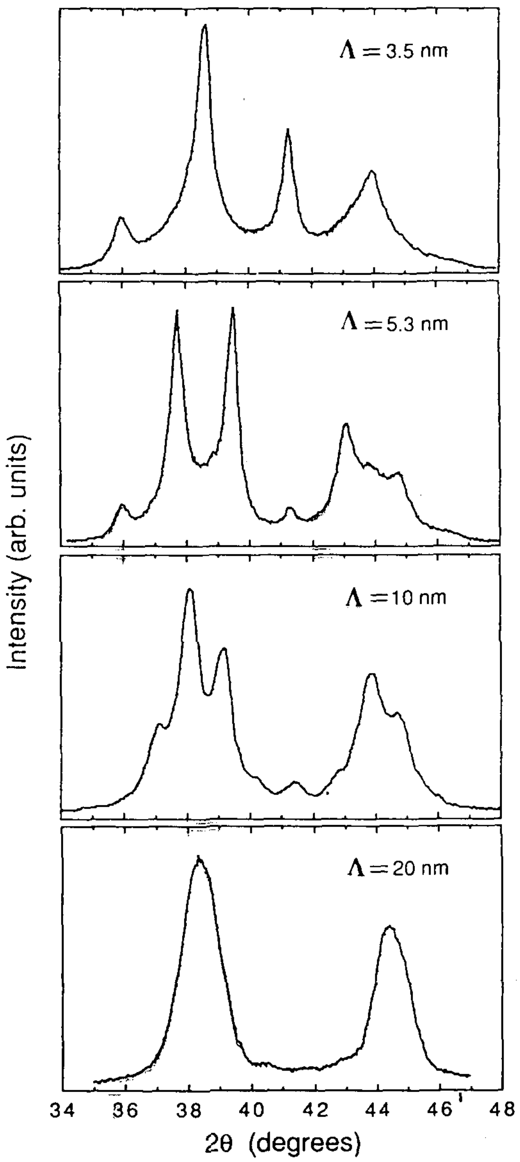

Fig. 4. X-ray diffraction spectra, prior to irradiation, for the modulation wavelengths used in this study.

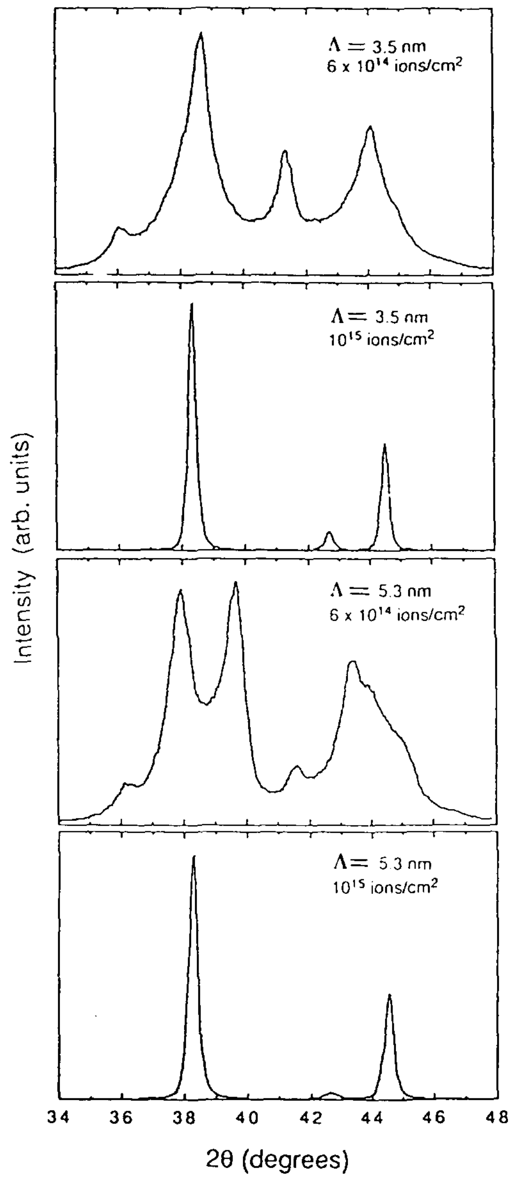

Fig. 5. X-ray diffraction spectra, at ion doses of 6×10^{14} and 10^{15} ions cm^{-2}, for the 3.5 and 5.3 nm modulation wavelength samples.

Samples irradiated at doses of 10^{13} and 10^{14} ions cm^{-2} show no measurable difference in both the θ–2θ scans and the rocking curves. X-ray spectra, at irradiation doses of 6×10^{14} and 10^{15} ions cm^{-2}, for the 3.5 and 5.3 nm wavelengths, are shown in Fig. 5. At 6×10^{14} ions cm^{-2}, the broadening of the superlattice peaks indicates a decrease in the coherence length normal to the layers. The value of $\bar{d}$ also decreases from 2.189 to 2.185 Å in the 3.5 nm sample, and from 2.186 to 2.172 Å in the 5.3 nm sample. The full width at half-maximum (FWHM) of the rocking curve changes by less than 5% at 6×10^{14} ions cm^{-2}. The shift in $\bar{d}$ is consistent with the assumption that the strain is being reduced with increasing ion dose. The phonon velocities at these doses were found to increase from 1.72 to 1.74 km s^{-1} in the 3.5 nm wavelength sample and from 1.73 to 1.87 km s^{-1} in the 5.3 nm wavelength sample. These results indicate a strong correlation between $\bar{d}$ and the shear elastic modulus. At a dose of 10^{15} ions cm^{-2}, there was no longer any evidence of superlattice structure and only well-oriented crystalline silver and cobalt peaks were observed. The dominant peaks were Ag(111) and Co(002), although a Co(100) peak was observed in some spectra. The crystallite sizes, as indicated by the peak widths, are greater than 25.0 nm.

The superlattice structure was maintained at higher doses for the $\Lambda = 10.0$ nm and 20.0 nm samples. The $\Lambda = 10$ nm superlattice showed superlattice peaks for all doses, except 10^{17} ions cm^{-2}. The resolution of the superlattice peaks decreases with increasing dose. Small shifts in $\bar{d}$ were observed in these samples, although uncertainties in these values preclude quantitative comparison with changes in phonon velocities. The $\Lambda = 20.0$ nm sample showed little change in the X-ray spectra at doses below 10^{15} ions cm^{-2}. At 10^{16} ions cm^{-2}, the layered structure is destroyed. Plotted in Fig. 6 is the Ag(111) peak and rocking curve FWHM, for this sample, which shows the reduction in the layered structure with increasing ion dose.

4. Summarizing remarks

Radiation damage induced by 6 MeV Si^{+} ion irradiation reproducibly reduces the anomalous softening in the shear elastic modulus of Ag/Co superlattice films of wavelengths from 3.5 to 20 nm. The phonon velocity of the superlattice films slowly increases until a wavelength-dependent critical dose is reached, at which time the phonon velocity rapidly increases to a value which is approximately the same for all wavelengths. The magnitude of the critical dose increases with increasing modulation wavelength. This indicates that the amount of energy needed to relieve the strain, in the Ag/Co system, is larger for the longer-wavelength superlattices. Consequently, a natural conclusion is that the strained region

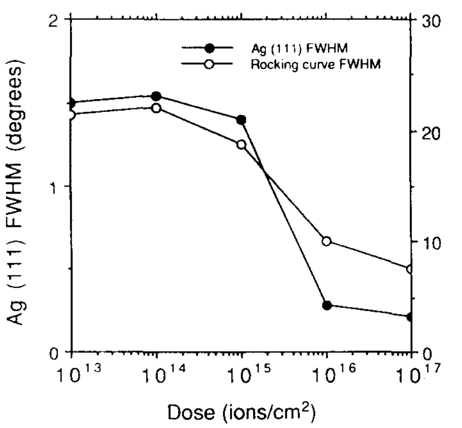

Fig. 6. Ag(111) peak and rocking curve FWHM values *vs.* irradiation dose for the 20.0 nm modulation wavelength sample.

increases with increasing superlattice wavelength and is not restricted to a fixed finite thickness from the interface.

The change in shear elastic modulus has been correlated with structural changes as characterized by X-ray spectra and rocking curve measurements. In unirradiated samples, the average lattice spacing increases with decreasing modulation wavelength and decreases with increasing irradiation dose. The measurements indicate that the origin of the elastic anomalies is due to the strains present. The origin of the strain, however, has not been determined and remains an interesting subject for future research.

Acknowledgments

This work was supported by the Office of Naval Research under Contract N00014-88K-0210 (at University of California, San Diego) and the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38 (at Argonne National Laboratory).

References

1 I. K. Schuller, in B. R. McAvoy (ed.), *Proc. Ultrasonics Symp.*, IEEE, New York, 1986, p. 1093.
M. Grimsditch, in M. Cardona and G. Guntherodt (eds.), *Light Scattering in Solids V*, Springer, Berlin, 1989, p. 285.
2 D. A. G. Bruggeman, *Ann. Phys. (Leipzig)*, *29* (1937) 160.
3 M. Grimsditch, *Phys. Rev. B*, *33* (1986) 3891.
4 J. S. Koehler, *Phys. Rev. B*, *2* (1970) 547.
5 L. R. Testardi, R. H. Willens, J. T. Krause, D. B. McWhan and S. Nakahara, *J. Appl. Phys.*, *52* (1981) 510.
6 W. M. C. Yang, T. Tsakalakos and J. E. Hillard, *J. Appl. Phys.*, *48* (1977) 866.
7 J. L. Lehoczky, *J. Appl. Phys.*, *49* (1978) 5479.
8 I. K. Schuller and A. Rahman, *Phys. Rev. Lett.*, *50* (1983) 1377.
9 M. Imafuku, Y. Sasajima, R. Yamamoto and M. Doyama, *J. Phys. F*, *16* (1986) 823.
10 A. Banerjea and J. Smith, *Phys. Rev. B*, *35* (1987) 5413.
11 R. C. Cammarata and K. Sieradzki, *Phys. Rev. Lett.*, *62* (1989) 2005.
12 A. F. Jankowsky, *J. Phys. F*, *18* (1988) 413.
13 D. Wolf and J. F. Lutsko, *Phys. Rev. Lett.*, *60* (1988) 1170.
14 B. M. Clemens and G. L. Eesley, *Phys. Rev. Lett.*, *61* (1988) 2356.
15 T. B. Wu, *J. Appl. Phys.*, *53* (1982) 5265.
16 P. C. Clapp, in T. Tsakalakos (ed.), *Modulated Structure Materials*, in *NATO Adv. Study Inst. Ser., Ser. E*, in the press.
17 W. E. Pickett, *J. Phys. F*, *12* (1982) 2195; to be published.

18 R. C. Cammarata, *Scr. Metall., 20* (1986) 479.

19 M. Grimsditch, *Superlattices Microstruct., 4* (1988) 677. M. Huberman and M. Grimsditch, *Phys. Rev. Lett., 62* (1989) 1403.

20 R. S. Nelson, *The Observation of Atomic Collisions in Crystalline Solids*, Wiley, New York, 1970.

21 V. M. Agranovich and V. V. Kirsanov, in R. A. Johnson and A. N. Orlov (eds.), *Physics of Radiation Effects in Crystals*, North-Holland, Amsterdam, 1986, p. 117.

22 M. Grimsditch, K. Gray, R. Bhadra, R. T. Kampwirth and L. Rehn, *Phys. Rev. B, 35* (1987) 833.

23 L. Rehn, P. Okamoto, J. Pearson, R. Bhadra and M. Grimsditch, *Phys. Rev. Lett., 59* (1987) 2987.

24 D. Gerlich, J. Holder and A. Granato, *Phys. Rev., 181* (1969) 1220.

25 E. Fullerton, R. Bhadra, W. Robertson, M. Grimsditch and I. K. Schuller, to be published.

26 S. M. Hues, R. Bhadra, M. Grimsditch, E. Fullerton and I. K. Schuller, *Phys. Rev. B, 39* (1989) 12966.

27 I. K. Schuller, *Phys. Rev. Lett., 44* (1980) 1597.

28 J. F. Ziegler, J. P. Biersack and U. Littmark, in J. F. Ziegler (ed.), *The Stopping and Range of Ions in Solids*, Pergamon, Oxford, 1985.

29 G. W. Farnell, in W. P. Mason and R. N. Thurston (eds.), *Physical Acoustics*, Vol. 6, Academic Press, New York, 1969, p. 109.

30 G. E. Henein and J. E. Hillard, *J. Appl. Phys., 55* (1984) 2895.

31 A. Kueny, M. Grimsditch, K. Miyano, I. Banerjee, C. M. Falco and I. K. Schuller, *Phys. Rev. Lett., 48* (1982) 166.

32 I. K. Schuller and M. Grimsditch, *J. Vac. Sci. Technol. B, 4* (1986) 1444.

33 D. B. McWhan, in L. L. Chang and B. Giessen (eds.), *Structure of Chemically Modulated Films in Synthetic Modulated Structures*, Academic Press, New York, 1985.

34 M. R. Khan, C. S. L. Chun, G. P. Felcher, M. Grimsditch, A. Kueny, C. M. Falco and I. K. Schuller, *Phys. Rev. B, 27* (1983) 7186.

35 J. L. Makous and C. M. Falco, *Solid State Commun., 68* (1988) 375.