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Effect of high-energy ion irradiation on the elastic moduli of Ag/Co superlattices

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The elastic moduli of Ag/Co superlattice structures have been studied by Brillouin scattering, as a function of irradiation with 6-MeV C^+ ions. A hardening of the superlattice structures with increasing dose was observed. These results imply that the elastic-constant anomalies in metallic superlattices are due to the strains present. The origin of the strains, however, cannot be uniquely identified.

The interest in the elastic properties of layered systems can be traced in the literature at least back to 1937. These initial calculations,[1] which treat each layer as a medium with elastic moduli C_{ij}, and many generalizations which followed[2] all show that the effective elastic constants of a composite system are given as some average of the moduli of the constituents. Moreover, in the long-wavelength limit, the elastic moduli of the system are shown to be independent of modulation wavelength, and depend only on the relative amounts of each material. In 1970 an article was published[3] in which it was suggested that a layered system composed of materials with dislocations could be stronger than that of its constituents. An effect of this nature was later indeed found[4,5] and was denoted as the "supermodulus" effect.[6]

The origin of the effect, however, is still controversial. Given that the C_{ij} of the composite system are sometimes greater than would be expected even for dislocation-free bulk material, the original ideas of Ref. 3 have not been pursued and have been replaced by a variety of other possible explanations. The proposed explanations can be divided into two general categories, structural[7–11] and electronic,[12–16] and we will not attempt to discuss them here except in the light of how our present results might affect each of the proposed mechanisms.

In order to address some of the issues relating to the origin of the supermodulus effect, we have performed structural and elastic-constant measurements on Ag/Co superlattices as a function of irradiation dose with 6-MeV C^+ ions. As previously found for many superlattices[6] we find that the elastic constants of Ag/Co *soften* with decreasing modulation wavelength. On the other hand, for a given modulation wavelength, the elastic constants *harden* with increasing radiation dose.

Ag/Co superlattices were prepared using magnetron sputtering, with a computer-controlled sample holder described earlier.[17] The Ar 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 $K\alpha$ radiation. Shear elastic constants were measured using Brillouin scattering with a 5+2 tandem Fabry-Pérot spectrometer. Using a National Electronics Corporation 950H Pelletron, the samples were irradiated with 6-MeV C^+ ions with doses of 2×10^{15} and 6×10^{15} ions/cm^2. It is known that at these energies the C^+ ions penetrate more than 1 μm into the film so that in the analysis of the Brillouin-scattering results, which probe approximately 500 nm into the film, stress effects resulting from primary-ion accommodation in the superlattice structure are not important.

A comprehensive investigation[18] of the modulation wavelength (Λ) dependence of the velocity (v) in Ag/Co shows that v in superlattices with $\Lambda \gtrsim 15$ nm is close to the value calculated using the bulk elastic properties of Ag and Co; below 15 nm the velocity decreases monotonically to a minimum at $\Lambda \simeq 2.6$ nm where it is $\sim 15\%$ lower than at long modulations. This behavior is shown by the filled circles in Fig. 1 which correspond to the velocities in three unirradiated samples with $\Lambda = 6.4$, 4.2, and 2.6 nm. The dashed line is the expected velocity according to classical continuum theories.[2] Also shown in Fig. 1 are the velocities measured in the same samples after irradiation with 2×10^{15} (open circles) and 6×10^{15} (squares) C^+ ions/cm^2.

The features to be noted in Fig. 1 are as follows: The irradiated samples revert towards the expected behavior and the velocities *increase* with radiation dose. This latter behavior is contrary to that reported for bulk metals[19,20] and inorganic-salt single crystals[21] where particle irradiation (and presumably the consequent defect production) *reduces* the elastic moduli.

The effect of C^+ irradiation on the high-angle diffraction spectra of Ag/Co superlattices is shown in Fig. 2; curves *a*, *b*, and *c* indicate doses of 0×10^{15}, 2×10^{15}, and 6×10^{15} ions/cm^2, respectively. The most important feature to note is that the spectra suffer only very minor changes as a function of dose. We point out that the

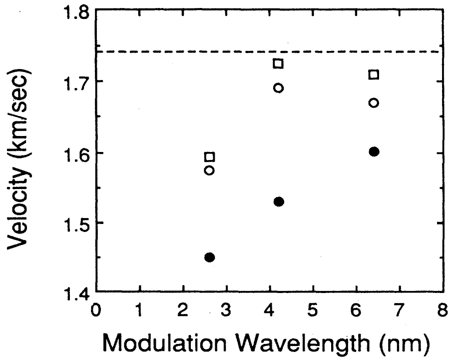

FIG. 1. Surface wave velocity in Ag/Co superlattices as a function of modulation wavelength and dose. Filled circles correspond to unirradiated samples, open circles and squares to those irradiated with 2×10^{15} and 6×10^{15} C^+ ions/cm^2, respectively. The dashed line is the velocity expected if the Ag and Co layers had the bulk values of their elastic moduli.

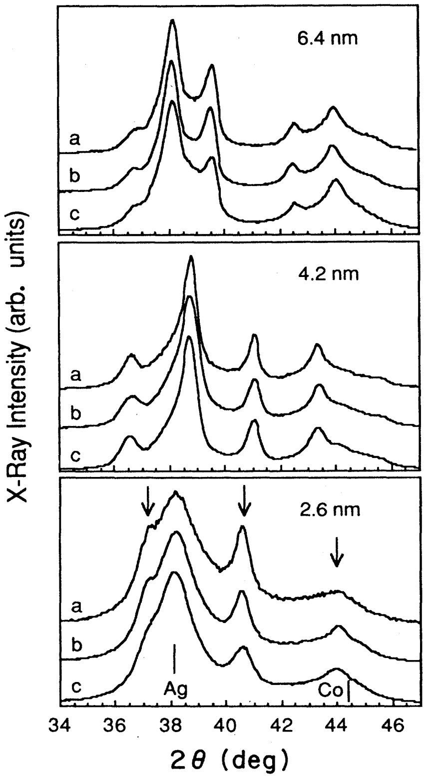

FIG. 2. X-ray spectra from three Ag/Co superlattices as a function of irradiation dose: curve *a*, unirradiated; curve *b*, 2×10^{15} C^+ ions/cm^2; and curve *c*, 6×10^{15} C^+ ions/cm^2. The 2.6-nm sample shows evidence for superlattice peaks (marked by arrows) and peaks at the bulk Ag and Co positions.

peaks in the spectra for the 4.2- and 6.4-nm samples are all superlattice peaks. In the spectrum for the 2.6-nm sample in addition to superlattice peaks (labeled by arrows) there are also peaks at the positions expected for bulk Ag and Co (labeled Ag and Co in the figure); this is an indication of imperfect layering, but again we stress that there are only minor changes after irradiation. Apart from the results shown in Fig. 2 we also performed rocking-curve measurements on the main peak of each spectrum; these also showed no change before and after irradiation.

Although it is not yet possible to make a quantitative analysis of x-ray spectra in terms of the width of the interfaces, intermixing, roughness, etc., it is known that the relative intensities of the superlattice peaks depend on the sharpness of the interfaces (e.g., square and sinusoidal composition modulations give rise to very different x-ray patterns).[22] The existence of superlattice peaks in all the spectra in Fig. 2 is a clear indication that the samples are layered; furthermore, the lack of appreciable changes in the relative intensities of the superlattice peaks is an indication that the sharpness of the interfaces is also being preserved. This latter fact is not unreasonable given the fact that Ag and Co are immiscible and no binary compound is known for them.[23]

It has been shown earlier[6] that many metallic superlattices exhibit large changes in their lattice-plane spacing perpendicular to the layering; preliminary results on Ag/Co[18] also show this to be the case. We shall refer to these changes as perpendicular strain ($S_\perp$). Experimentally $S_\perp$ has also been shown to correlate with the elastic anomalies. A molecular dynamics simulation, which assumes the strain to be distributed throughout each layer, was also able to reconcile quantitatively the elastic softening with $S_\perp$ in Ni/Mo.[24] It is therefore tempting to assign the present results to release of the strain by the ion irradiation.

Uncertainties in the x-ray results (due to the time span elapsed between measurements on irradiated and unirradiated samples) precludes the possibility of measuring the small changes in the average lattice spacing. However, channeling experiments[25] on Mo/W superlattices show that strains are indeed relaxed by ion irradiation, thus reinforcing the experimental fact that elastic anomalies and strains are closely interrelated. It does not, however, explain whether the origin of the strains is structural or electronic.

How are the results presented here accommodated within the framework of the proposed explanations for the supermodulus effect? The most serious drawback in any interpretation of the results is that it is not clear what structural rearrangements are being produced by the irradiation. For example, if it is assumed that the effect of the irradiation is to anneal the parallel strains at each interface ($S_\parallel$), then structural models imply that a reduction in $S_\parallel$ produces (via Poisson's ratio) a reduction in $S_\perp$ and also concomitant reductions of the elastic anomaly. If, on the other hand, it is assumed that additional defects are introduced into the material then the electronic-nesting explanations[12,14] might also be expected to produce a reduction of the anomaly. Finally, if it is assumed that there is some bulk mixing between the Ag and Co layers due to head-on collisions of the incident C^+ ions, then the electron-transfer-based models[16] also predict a disappearance of $S_\perp$ and consequently also of the supermodulus effect.

For the above reasons, unless more information can be obtained about the nature of the "damage" produced during irradiation, the experiments reported here are not capable of distinguishing between the proposed explanations. The arguments given above, however, do provide interesting predictions regarding the temperature dependence of the elastic anomalies. In systems that do not form alloys, temperature annealing will reduce the number of defects and relax interfacial strains, but will not produce "bulk" mixing of the layers. Therefore structural models would be consistent with a *reduction* of the anomalies as temperature is raised; electronic nesting models might predict an *increase* in the effect, while those based on electronic transfer would be more consistent with no effect. (We stress that these predictions only hold for immiscible materials; in compositionally modulated systems annealing will destroy the superlattice nature of the samples.)

In conclusion, we have shown that irradiation of Ag/Co superlattices with C^+ ions has the effect of decreasing the elastic anomalies introduced by the layering. Although the results do not allow the unique identification of the mechanism responsible for the supermodulus effect, they do allow predictions to be made regarding the temperature dependence of the effect. These predictions are different for the various models proposed in the literature.

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[1] D. A. G. Bruggeman, Ann. Phys. (Leipzig) **29**, 160 (1937).

[2] For a list of previous calculations, see references in M. Grimsditch, Phys. Rev. B **33**, 5891 (1986).

[3] J. S. Koehler, Phys. Rev. B **2**, 547 (1970).

[4] W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **48**, 876 (1977).

[5] J. L. Lehoczky, J. Appl. Phys. **49**, 5479 (1978).

[6] For a review, see I. K. Schuller, in *Proceedings of the IEEE 1985 Ultrasonics Symposium,* edited by B. R. McAvoy (IEEE, New York, 1986), p. 1093; or M. Grimsditch, in *Light Scattering in Solids V,* edited by M. Cardona and G. Güntherodt (Springer-Verlag, Heidelberg, 1989).

[7] M. Imafuku, Y. Sasajima, R. Yamamoto, and M. Doyama, J. Phys. F **16**, 823 (1986).

[8] A. Banerjea and J. Smith, Phys. Rev. B **35**, 5413 (1987).

[9] A. F. Jankowsky, J. Phys. F **18**, 413 (1988).

[10] D. Wolf and J. E. Lutsko, Phys. Rev. Lett. **60**, 1170 (1988).

[11] B. M. Clemens and G. L. Eesley, Phys. Rev. Lett. **61**, 2356 (1988).

[12] T. B. Wu, J. Appl. Phys. **53**, 5265 (1982).

[13] P. C. Clapp, in *Modulated Structure Materials,* edited by T. Tsakalakos, NATO Advanced Study Institute, Series E (Nijhoff, Dordrecht, 1984), Vol. 83, p. 455.

[14] W. E. Pickett, J. Phys. F **12**, 2195 (1982); and (unpublished).

[15] R. C. Cammarata, Scr. Metall. **20**, 479 (1986).

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

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

[18] E. Fullerton, R. Bhadra, W. Robertson, M. Grimsditch, and I. K. Schuller (unpublished).

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

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

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

[22] See, for instance, a chapter in *Physics, Fabrication and Applications of Multilayered Structures,* edited by P. Dhez and C. Weisbuch (North-Holland, Amsterdam, in press).

[23] See, for instance, M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), p. 16.

[24] I. K. Schuller and A. Rahman, Phys. Rev. Lett. **51**, 498 (1983).

[25] S. Mantl, D. B. Poker, and K. Reichet, Nucl. Instrum. Methods Phys. Res., Sect. B **19-20**, 677 (1987).