PHYSICAL REVIEW B VOLUME 31, NUMBER 6 15 MARCH 1985

State of Si and Sn in glassy Au alloys

E. Huber and M. von Allmen
Institute of Applied Physics, University of Bern, CH-3012 Bern, Switzerland
(Received 29 October 1984)

Glassy films of Au-Sn were prepared by laser quenching with ns pulses in the composition range from 12 to 81 at. % Sn. Electrical resistivity was measured during annealing from 170 to 370 K and crystallization temperatures were determined. These properties are compared to those of glassy films of Au-Si investigated earlier as well as to those of vapor-quenched amorphous phases of the same systems. The resistivities of Au-Si and Au-Sn glasses are remarkably similar in the composition range up to 30 at. % Si or Sn. In this range Si is believed to be in a metallic state. The resistivity of disordered metallic Si is estimated as 82±8 $\mu\Omega$ cm. The stability of the Au-rich Si and Sn glasses are shown to be inversely correlated with the density of states at the Fermi level.

I. INTRODUCTION

Laser quenching with its high cooling rates[1] is able to produce binary glassy alloys over extended ranges of composition. We have previously employed this method to study the electronic properties of the system Au-Si.[2,3] Preliminary results on Au-Sn have been published recently.[4] In the present paper we report new findings for laser-quenched Au-Sn alloys and compare them to the earlier Au-Si results,[3] as well as to literature data for vapor-quenched Au-Sn and Au-Si.[5–10] Finally, relations between the two systems considered are used to draw conclusions about the metallic state of Si and the density of states at the Fermi level for Au-rich Si and Sn glasses.

II. EXPERIMENTAL METHOD

Samples were prepared by electron-gun deposition of alternating layers of Au and Sn onto sapphire substrates in a ultrahigh-vacuum chamber (better than 10^{-7} mbar). The thicknesses of individual layers were chosen such as to yield the desired mean composition after laser melting and interdiffusion. In order to ensure homogeneous mixing, individual layers were made no more than 35 nm thick. Overall thickness was 150 nm. These structures were irradiated with 50 ns pulses from a Nd:yttrium aluminum garnet laser. With these parameters relevant cooling rates are of the order of 10^9 K/s.[1] During irradiation the samples were kept in a vacuum chamber with a vacuum better than 10^{-2} mbar and at temperatures between 150 and 170 K. Resistivity measurements were done between 150 and 370 K *in situ* without breaking the vacuum. Film temperature was controlled using peltier cooling and resistance heating. For the resistivity measurements the standard four-point probe method was used.

III. RESULTS AND DISCUSSION ON Au-Sn

As-irradiated films of all compositions tried (between 12 and 81 at. % Sn) were found to be glassy. The amorphous-crystalline phase transition manifests itself by a rather abrupt drop of the resistivity at the transition temperature T_{ac} as shown in Fig. 1. The presence of this drop is taken as evidence for the amorphousness of the as-irradiated films in the present work. Crystallized films could easily be returned to the glassy state by cooling below T_{ac} and reirradiating *in situ*.

For some film compositions the resistivity showed a second and less pronounced step when the temperature was increased beyond T_{ac}. This step is barely visible in the trace 68 at. % Sn of Fig. 1 (zero-point suppression was used to detect these steps clearly). Although x-ray diffraction could not be performed at low temperature, we take this second step as an indication that crystallization of the glass results in a metastable intermediate phase, the decay of which produces the additional step. The phenomenon occurred for compositions between 34 and 70 at. % Sn (most pronounced between 50 and 60 at. % Sn). It was verified by x-ray diffraction that an equilibrium configuration was reached at 370 K. The time scale for complete crystallization at 370 K is typically 1 h. It may be mentioned that Au-Si glasses also form a metastable crystal which decays into the equilibrium phases at about 420 K.[2]

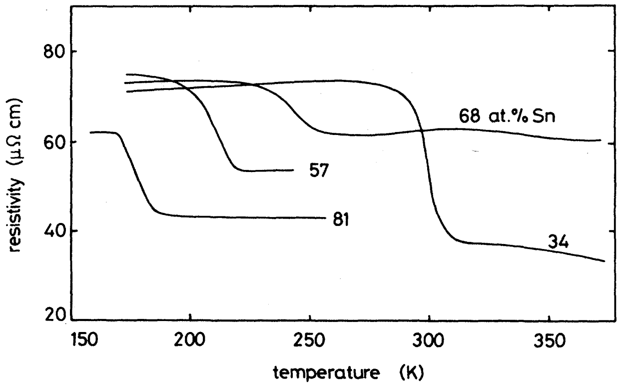

FIG. 1. Change of the electrical resistivity of laser-quenched Au-Sn glasses during annealing at a rate of temperature rise of 3 K/min.

Figure 2 shows the transition temperature T_{ac} of Au-Sn glasses as a function of composition. Crystallization temperatures for laser-quenched Au-Si glasses[3] as well as for vapor-quenched amorphous Au-Sn films[7] (dashed line) are included for comparison. Arrows indicate the composition of stable phases in the system. It is apparent from Fig. 2 that the stability of the Au-rich glasses increases strongly with Sn content (a similar increase can be seen for Au-Si), reaching a maximum at about 30 at. % Sn. In Sec. V we will show that the stability in this range is correlated with the density of states at the Fermi level.[11] The decrease of T_{ac} above 30 at. % Sn is probably related to the formation of the metastable crystal mentioned earlier.

Figure 3 shows the resistivities of the glassy Au-Sn films as a function of composition, measured at 170 K or below. Also shown for comparison are resistivities of laser-quenched Au-Si and vapor-quenched (dashed lines) amorphous Au-Si and Au-Sn films. The curves pertaining to vapor-quenched amorphous phases are averaged values taken from different authors (Refs. 5, 6, and 10 for Au-Si and Refs. 7 and 8 for Au-Sn); the extent of scatter in the data is indicated by the error bars. The range of resistivities of AuSn single crystals at 230 K observed under various crystallographic directions[12] is indicated by an open vertical bar. The electrical resistivities of the laser-quenched glasses show a minimum around 50 at. % Sn. This is not observed in vapor-quenched films. A possible explanation for the occurrence of the minimum is the presence of short-range order in the glass, perhaps related to that of the AuSn compound. There is experimental evidence for short-range order also in liquid Au-Sn.[13]

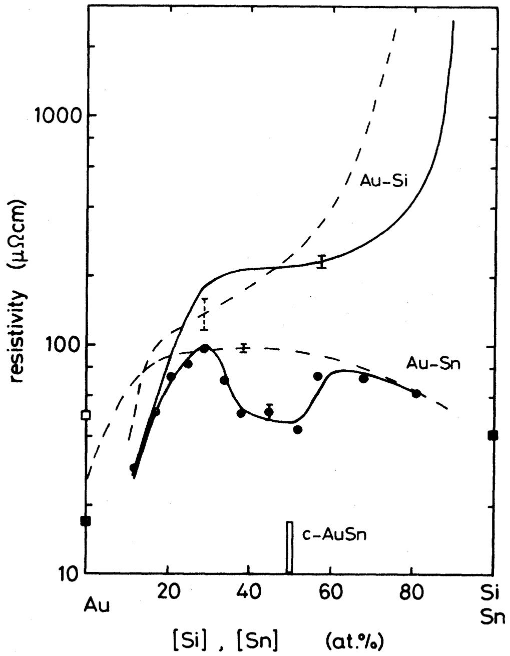

FIG. 3. Electrical resistivity as a function of composition. Closed circles and solid lines: laser-quenched Au-Sn (this work) and Au-Si (Ref. 3); dashed lines: vapor-quenched Au-Sn (Refs. 7 and 8) and Au-Si (Refs. 5, 6, and 10); closed squares: elemental melt values extrapolated to room temperature; open square: amorphous Au (Ref. 16). The open vertical bar gives the range of resistivities observed for single-crystalline AuSn at various orientations and at 230 K.

For very Au-rich compositions (less than 25 at. % Sn) the electrical resistivities of vapor-quenched films are clearly higher than those of laser-quenched films. This is also true for Au-Si films. The probable reason is the incorporation of gases and other impurities during vapor quenching. However, as long as the films remain metallic, the resistivity of vapor-quenched films can exceed that of laser-quenched ones only while below Mooij's saturation resistivity[14] (a further increase in resistivity would indicate a change in the regime of conduction[15]). The saturation value is apparently reached around 30 at. % Sn where both kinds of Au-Sn films have equal resistivities. The effect of impurity on resistivity is most evident for amorphous Au, which can be produced by vapor deposition at 25 K in an atmosphere of He.[16] The large amount of He incorporated [between 10 and 46 at. % (Ref. 16)] explains the discrepancy between the resistivities of "amorphous" Au (from Ref. 16, open square in Fig. 3) and "glassy" Au (approximated by extrapolating the liquid resistivity down to room temperature, closed square in Fig. 3). As for the case of pure Sn, the extrapolation of the liquid resistivity to room temperature is consistent with the resistivities of both the laser- and vapor-quenched alloys extrapolated to pure Sn (see Fig. 3).

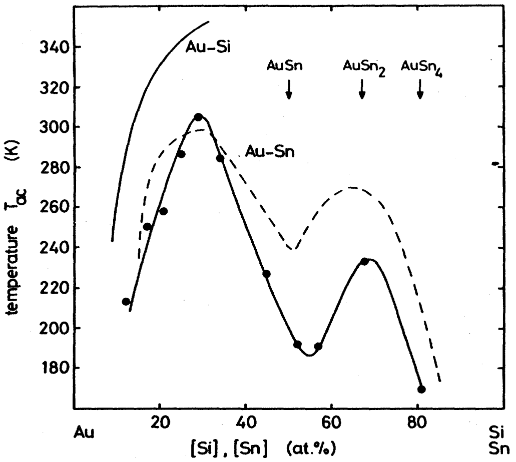

FIG. 2. Amorphous-crystalline transition temperature T_{ac} as a function of composition. Closed circles and solid lines: laser-quenched Au-Sn (this work) and Au-Si (Ref. 3); dashed line: vapor-quenched Au-Sn (Refs. 7 and 8). Arrows indicate the compositions of equilibrium compounds.

The temperature coefficients of resistivity (TCR's) at 170 K of laser-quenched Au-Sn glasses are minimum around 28 at. % Sn. This is consistent with Mooij's correlation between resistivity and TCR for disordered metallic alloys.[14] The measured minimum value of the TCR's of laser-quenched films was -1×10^{-4} K^{-1}, which is about halfway between the TCR's of vapor-quenched films (-1.8×10^{-4} K^{-1}) and of the liquid (approximately zero, depending on temperature).[7]

IV. THE METALLIC STATE OF SI

A metallic state of Si in disordered noble-metal alloys has been postulated by several authors.[3,6,17,18] In the present discussion we attempt to use the similarities between the Au-Si and Au-Sn glasses found in this work to further substantiate this postulate and to calculate the resistivity of metallic Si. Si and Sn are closely related elements: Si, normally semiconducting with a diamond structure, becomes metallic with a β-tin structure under high pressure[19] or disordered metallic in the liquid[20] while Sn, normally metallic (β tin), becomes semiconducting with a diamond structure at low temperature. In the glassy Au alloys Si and Sn yield very similar resistivity-versus-composition curves up to about 30 at. % (Fig. 3). This similarity also holds in the liquid alloys.[13,21]

In the following we present three approaches to estimate the resistivity of disordered solid metallic Si (DSM Si) on the basis of the known resistivity of amorphous Sn (liquid extrapolated to room temperature, or glassy Au-Sn extrapolated to pure Sn). All these approaches rely on relations between the resistivities of the alloy systems Au-Si and Au-Sn. Table I lists values for the resistivity of DSM-Si obtained by the three approaches as described in the following.

The first approach is based on a correlation we found to hold in *liquid N-S systems,* where N stands for a noble metal and S for Si, Ge, In, Ga, or Sn. The data were taken from Refs. 21, 13, 16, and 22. For all these systems the resistivities as a function of S content behave very similarly on the N-rich side. We found that the following empirical relation holds fairly well:

$$\frac{\rho_A}{\rho_{\mathrm{Sn}}} \simeq 1.2 \left| \frac{\rho_{N\text{-}A}}{\rho_{N\text{-}\mathrm{Sn}}} \right|_{x \simeq 0.3,\ \text{melting point}} , \tag{1}$$

where A stands for Si, Ge, In, or Ga and x is the concentration of A and Sn (expressed in atomic fraction). The empirical factor 1.2 is the mean of values between about 1.0 (for the low-melting In and Ga) and about 1.4 (for Si and Ge) and arises from the huge differences between the melting points of the elements considered. We now assume that the relation (1) also holds in the glassy state at room temperature, but with the factor 1.2 omitted. The data of Fig. 3 thus allows calculation of the resistivity of metallic Si. The result is given in the first column of Table I.

The second approach is to use the concentration dependence $\rho(x)$ of the electrical resistivities of *solid solutions*[23] of Sn and Ge in Au. We assume the following relation to hold:

$$\frac{\rho_{\mathrm{Si}}}{\rho_{\mathrm{Sn}}} = \frac{(\partial\rho/\partial x)_{\text{Au-Si}}}{(\partial\rho/\partial x)_{\text{Au-Sn}}} , \tag{2}$$

where on the right-hand side the resistivities are those of the solid solutions of Si and Sn in Au. Since, unfortunately, a solid solution of Si in Au does not exist in equilibrium, we use the data for Ge and scale it using the ratio of the liquid-state resistivities

$$(\partial\rho/\partial x)_{\text{Au-Si}} = \frac{\rho_{l\text{-Si}}}{\rho_{l\text{-Ge}}} (\partial\rho/\partial x)_{\text{Au-Ge}} . \tag{3}$$

This allows us to calculate the resistivity of metallic Si. The result is given in the second column of Table I.

TABLE I. Resistivity of disordered solid metallic Si (DSM Si) as calculated from three different approaches as described in the text.

Approach	Result ($\mu\Omega$ cm)
(1) Liquid	83
(2) Solid solution	79
(3) EMT	83
Mean	82

The third approach is to use the *effective-medium theory* (EMT) (see Ref. 24). To describe the conductivity $\sigma(x)$ of Au-Si or Au-Sn as a function of composition we try the following separation ansatz:

$$\sigma(x) = \sigma_{\mathrm{mix}}(x) + \sigma_i(x) , \tag{4}$$

where $\sigma_{\mathrm{mix}}(x)$ accounts for the effect of mere mixing, to be treated by EMT, and $\sigma_i(x)$ describes some unknown interaction which we take to be the same for Si and Sn. The conductivity $\sigma_{\mathrm{mix}}(x)$ of a mixture between a good conductor (the solvent) and a bad one (the solute) is a linear function of x (the solute content) for x smaller than about 0.4. This result follows from the formulas of EMT given in Ref. 24. Hence, we write

$$\sigma_{\mathrm{mix}}(x) = \sigma_0 + sx , \tag{5}$$

where σ_0 is the solvent conductivity and s is a function of the conductivities of both species as well as of the coordination number. Applying (4) and (5) to the systems Au-Si and Au-Sn we can express the difference of their conductivities $\Delta\sigma(x) = \sigma_{\text{Au-Sn}}(x) - \sigma_{\text{Au-Si}}(x)$ as

$$\Delta\sigma(x) = (s_{\mathrm{Sn}} - s_{\mathrm{Si}})x , \tag{6}$$

where the expression $(s_{\mathrm{Sn}} - s_{\mathrm{Si}})$ depends only on the properties of the *pure* constituents: For the resistivities the values of the liquids extrapolated to room temperature (17 $\mu\Omega$ cm for Au and 41 $\mu\Omega$ cm for Sn) are used and the coordination number of both Au-Si and Au-Sn is assumed to be 10.[9] $\Delta\sigma(x)$ as taken from Fig. 3 turns out to follow a straight line, allowing determination of the slope $(s_{\mathrm{Sn}} - s_{\mathrm{Si}})$ and hence the resistivity of metallic Si. The result is given in the third column of Table I. The last column of Table I gives the mean of the three estimates discussed above. Even admitting that the close agreement of the values found is somewhat fortuitous, we feel encouraged to take it as evidence for the metallic state of Si in the Au-rich glasses. The most probable value for the resistivity of metallic Si from Table I is 82 $\mu\Omega$ cm with an estimated error of 10%.

V. DENSITY OF STATES

Nagel and Tauc[11] have proposed that the stability of N-S glasses (where N stands for a noble or transition metal and S for a group-IV or -V element) is correlated with the occurrence of a *minimum* in the density of states (DOS) at the Fermi level, $N(E_F)$. Moruzzi *et al.*[25] have recently argued that in transition-metal glasses high stability is correlated with a *high* $N(E_F)$, in contrast to the Nagel and Tauc criterion. Recent photoemission measurements on vapor-quenched Au-Sn amorphous phases by Häussler *et al.*[26] revealed a correlation in the sense of Nagel and Tauc. In what follows we show that $N(E_F)$ can be estimated from resistivity data and we apply the method to our glasses from 12 to 30 at. % Si or Sn. In view of the results of Sec. IV we take the Si to behave as a metal (DSM-Si) with a resistivity of 82 $\mu\Omega$ cm and assume that the interaction between DSM-Si and Au is the same as that between Sn and Au.

Mott and Davies[15] introduced five different regimes of conduction for liquid metallic and semiconducting systems. In regime I (mean free path larger than the interatomic distance, $30\ \mu\Omega\,\mathrm{cm} < \rho < 200\ \mu\Omega\,\mathrm{cm}$) the conductivity σ is given by

$$\sigma=\frac{e^2}{12\pi^3\hbar}S_F L g^2 , \qquad (7)$$

where S_F is the Fermi surface area and L is the mean free path. The factor g was introduced by Mott as

$$g=\frac{N(E_F)}{N(E_F)_{\text{free-electron metal}}} . \qquad (8)$$

In regime II Eq. (7) still holds with L equal to the interatomic distance and $1/\sigma$ equal to the saturation resistivity. Equation (7) can be written as

$$\sigma=Rn\tau g^2 , \qquad (9)$$

where n is the number of free electrons per atom, τ is the relaxation time, and R is a numerical constant. For an ideal metal or for a mixture of noninteracting ideal metals g is equal to 1. Such a mixture can be described by EMT and we denote its conductivity, as before, by $\sigma_{\text{mix}}(x)$,

$$\sigma_{\text{mix}}(x)=Rn(x)\tau_{\text{mix}}(x) . \qquad (10)$$

If there is interaction between the two metals $g(x)$ will differ from 1 and the relaxation time $\tau(x)$ will be of the form

$$1/\tau(x)=1/\tau_{\text{mix}}(x)+1/\tau_i(x) , \qquad (11)$$

where i denotes interaction. The conductivity can now be written as

$$\frac{1}{\sigma(x)}=\frac{1}{Rn(x)g^2(x)}[1/\tau_{\text{mix}}(x)+1/\tau_i(x)] . \qquad (12)$$

Expressions (10) and (12) are now applied to the systems Au-Si and Au-Sn. Since we assumed the interactions to be the same for Si and Sn, we can express the difference of the resistivities $\Delta\rho(x)=\rho_{\text{Au-Si}}(x)-\rho_{\text{Au-Sn}}(x)$ as

$$\Delta\rho(x)=\frac{1}{g^2(x)}\left[\frac{1}{\sigma_{\text{mix,Au-Si}}(x)}-\frac{1}{\sigma_{\text{mix,Au-Sn}}(x)}\right] . \qquad (13)$$

Using (5) we find

$$\Delta\rho(x)=\frac{1}{g^2(x)}\left[\frac{1}{s_{\text{Si}}x+\sigma_0}-\frac{1}{s_{\text{Sn}}x+\sigma_0}\right] , \qquad (14)$$

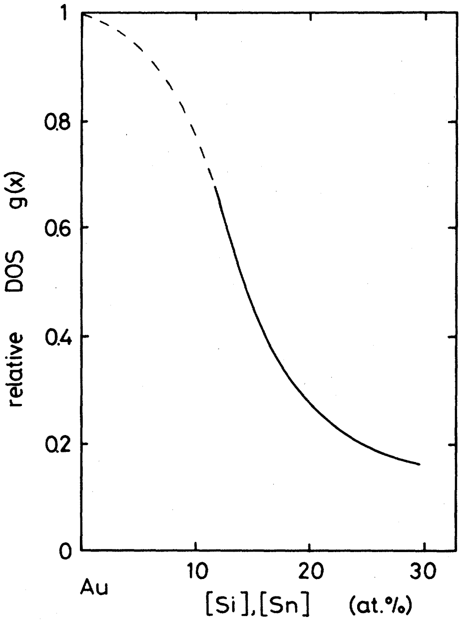

FIG. 4. Relative DOS $g(x)=N(E_F)/N(E_F)_{\text{free-electron metal}}$ as described in the text.

where s_{Si}, s_{Sn}, and σ_0 are the parameters of EMT used in Eqs. (4) and (5) and $\Delta\rho(x)$ is taken from Fig. 3. The reduction of the actual $N(E_F)$ relative to the free-electron value as expressed by $g(x)$ is plotted in Fig. 4. It can be seen to decrease sharply with Si or Sn content up to about 25 at. % and to remain roughly constant on a low level above this value. This means that our $N(E_F)$ is inversely related to glass stability on the Au-rich side (Fig. 2), as predicted by the theory of Nagel and Tauc.

VI. SUMMARY AND CONCLUSIONS

With laser quenching at 10^9 K/s glassy Au-Sn alloys can be produced in the range of at least 12–81 at. % Sn. The resistivities of the glassy alloys tend to be lower than those of vapor-quenched ones of the same composition. The resistivities show the general behavior expected for disordered metallic alloys of this kind[21] at all compositions except for the glasses around 50 at. % Sn, where short-range order is believed to influence the resistivity. This indicates that laser quenching, being a form of melt quenching, tends to preserve structures present (or prepared) in the liquid phase. A comparison between glassy Au-Sn and Au-Si has shown clear evidence for the metallic state of Si in Au-rich alloys. The resistivity of the disordered solid metallic Si (DSM-Si) is estimated as $82\pm8\ \mu\Omega$ cm. The concentration dependence of the stability of Au-rich glasses (up to 30 at. % Si or Sn) is shown to be correlated with a decreasing DOS at E_F.

ACKNOWLEDGMENTS

We thank U. Kambli and N. Baltzer for helpful discussions and Professor H. P. Weber for interest and support. Technical assistance by R. Flück and A. Blatter is gratefully acknowledged. This work was supported, in part, by the Swiss Commission for the Encouragement of Scientific Research.

[1] A. Blatter, M. von Allmen, and E. Huber, in *Amorphous Metals—Nonequilibrium Processing,* Material Research Society (Europe) Conference Proceedings, edited by M. von Allmen (Editions de Physique, Paris, 1984), p. 74; M. von Allmen, in *Glassy Metals II,* Vol. 53 of *Topics in Applied Physics,* edited by H. Beck and H.-J. Güntherodt (Springer, Heidelberg, 1983), p. 261.

[2] M. von Allmen, S. S. Lau, M. Mäenpää, and B. Y. Tsaur, Appl. Phys. Lett. **36**, 205 (1980).

[3] E. Huber and M. von Allmen, Phys. Rev. B **28**, 2979 (1983).

[4] E. Huber and M. von Allmen, in *Amorphous Metals—Nonequilibrium Processing,* Material Research Society (Europe) Conference Proceedings, edited by M. von Allmen (Editions de Physique, Paris, 1984), p. 343.

[5] P. Mangin, G. Marchal, C. Mourey, and C. Janot, Phys. Rev. B **21**, 3047 (1980).

[6] J. J. Hauser and J. Tauc, Phys. Rev. B **17**, 3371 (1978).

[7] P. Häussler and F. Baumann, Z. Phys. B **49**, 303 (1983).

[8] E. Blasberg, D. Korn, and H. Pfeifle, J. Phys. F **9**, 1821 (1979).

[9] H. Leitz, Z. Phys. B **40**, 65 (1980).

[10] N. Nishida, M. Yamaguchi, T. Furubayashi, K. Morigaki, H. Ishimoto, and K. Ono, Solid State Commun. **44**, 305 (1982).

[11] S. R. Nagel and J. Tauc, Phys. Rev. Lett. **35**, 380 (1975).

[12] J.-P. Jan, W. B. Pearson, A. Kjekshus, and S. B. Woods, Can. J. Phys. **41**, 2252 (1963).

[13] H. A. Davies and J. S. Llewelyn Leach, Philos. Mag. **19**, 1271 (1969).

[14] J. H. Mooij, Phys. Status Solidi A **17**, 521 (1973); P. J. Cote and L. V. Meisel, in *Glassy Metals I,* Vol. 46 of *Topics in Applied Physics,* edited by H.-J. Güntherodt and H. Beck (Springer, Heidelberg, 1982), p. 141.

[15] N. F. Mott and E. A. Davies, in *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979), Chap. 5.

[16] J. J. Hauser, R. J. Schutz, and W. M. Augustyniak, Phys. Rev. B **18**, 3890 (1978).

[17] A. Hiraki, A. Shimizu, and M. Iwami, Appl. Phys. Lett. **26**, 57 (1975).

[18] B. Stritzker and H. Wühl, Z. Phys. **243**, 361 (1971).

[19] S. Minomura, J. Phys. (Paris) Colloq. Suppl. 10 **42**, C4-181 (1981).

[20] M. Davidovic, M. Stoijc, and Dj. Jovic, J. Phys. C **16**, 2053 (1983).

[21] G. Busch and H.-J. Güntherodt, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1974), Vol. 29, p. 235.

[22] Ch. Holzhey, H. Coufal, G. Schubert, J. Brunnhuber, and S. Sotier, Z. Phys. B **33**, 25 (1979).

[23] References cited in *Landolt Börnstein, New Series* (Springer, Berlin, 1982), Vol. 15a.

[24] S. Kirkpatrick, Phys. Rev. Lett. **27**, 1722 (1971).

[25] V. L. Moruzzi, P. Oelhafen, and A. R. Williams, Phys. Rev. B **27**, 7194 (1983).

[26] P. Häussler, F. Baumann, J. Krieg, G. Indlekofer, P. Oelhafen, and H.-J. Güntherodt, Phys. Rev. Lett. **51**, 714 (1983).