Pergamon

Solid State Communications, Vol. 96, No. 6, pp. 391–396, 1995

0038–1098/95 $9.50 + .00

0038–1098(95)00365-7

CHARACTERIZATION OF EPITAXIAL *a* AXIS AND *c* AXIS ORIENTED $YBa_2Cu_3O_{7-x}$ THIN FILMS. EFFECT OF UNIAXIAL STRESSES

S. Sanfilippo and J. Beille

Laboratoire L. Néel, C.N.R.S., BP 166, 38042 Grenoble, Cedex 09, France

F. Pourtier and J.C. Villegier

L.E.T.I., C.E.N.G., 38054 Grenoble, Cedex 09, France

D. Chateigner, P. Germi and M. Pernet

Laboratoire de Cristallographie, C.N.R.S., BP 166, 38042 Grenoble, Cedex 09, France

and

H. Noël

Laboratoire de Chimie Minérale, Univ. de Rennes, Av. Gl Leclerc, 35042 Rennes, Cedex 09, France

(*Received* 29 *March* 1995; *accepted in revised form* 24 *May* 1995 *by P. Burlet*)

The effects of uniaxial stresses on *c* axis as well as *a* axis oriented thin films of $YBa_2Cu_3O_{7-x}$ have been investigated. We show that the effects depend strongly on the microstructure. Thus the *a* axis oriented films exhibit non monotonous uniaxial pressure effects. On the contrary, *c* axis oriented films show reversible effects. Our results are compared with those previously published.

Keywords: A. high-T_c superconductors, A. thin films, B. epitaxy, D. electronic transport, E. strain, high pressure.

1. INTRODUCTION

EXPERIMENTS under uniaxial stresses are important in order to understand the anisotropic properties of the high T_c superconductors. Such measurements have already been carried out [1–3]. In this work, we intended to examine to what extent the effects of uniaxial stresses are sample dependant for $YBa_2Cu_3O_{7-x}$ films of "epitaxial quality", to establish if reliable intrinsic values of $dT_c/d\sigma_{a,b}$ (where $\sigma_{a,b}$ is a stress in the *a*, *b* plane) as well as $dT_c/d\sigma_c$ (where σ_c is a stress along the *c* axis) can be driven from such experiments.

2. EXPERIMENTAL DETAILS

2.1. *Samples*

Films of $YBa_2Cu_3O_{7-x}$ were sputtered onto (1 0 0) oriented single crystal $SrTiO_3$ substrates in a conventional DC magnetron sputtering system. *c* axis oriented films were obtained using a deposition temperature of 850°C. The *a* axis oriented samples were prepared using a two step deposition process: one step at 700°C and the second at 850°C. We investigated *c* axis oriented films of 900 (T298) and 1800 Å (T351) thickness and one *a* axis oriented film of 2000 Å (T450P) thickness.

In order to interpret the effects of pressure, the knowledge of the O-content is important. However, due to the small size of the samples, it was not possible to use direct methods, such as thermogravimetry or iodometry. We have estimated the O-content from electrical transport properties and *c* parameter measurements in the usual way.

The epitaxial quality of the *c* axis films was confirmed using X-ray measurements: pole figures, ϕ-scan, Ω-scan (rocking curves), by electron microscopy and also by using measurements of the canalisation rate in RBS experiments. Electrical transport properties were also investigated. These films exhibit a metallic normal state behaviour with a ratio $\rho(300\,K)/\rho(100\,K) \approx 3$, onset superconducting critical temperatures $T_{c,on}$ of about 92 K, off-set critical temperatures $T_{c,off} \cong 89.5$–90 K with a transition width of about 2 K, and a resistivity $\rho(100\,K) < 80\,\mu\Omega$ cm. The value of the c parameter obtained by refinement on several homologous diffraction lines is 11.695 and 11.700 Å for the films T298 and T351 respectively. The oxygen content has previously been correlated to the values of T_c and c [4–6]. The T_c values reported in [4, 5], determined by a.c. susceptibility measurements, should be compared with our offset resistive determinations of T_c. On the basis of Table 2, and from the values of T_c and c, the oxygen content of our c axis films is determined to be 6.8–6.85.

Moreover the microstructure of the c axis films has been determined from HRTEM studies: the films are made of oriented grains of size 2000–5000 Å [7].

For the a axis oriented film (T450P) the normal state resistance exhibits a small decrease vs temperature with a ratio $R(300\,K)/R(100\,K) = 1.15$. We estimated the resistivity of such films to be ≈20 times larger than the average value of the c axis oriented films; their transition width is larger (10 K). The value of the c parameter from X-ray diffraction experiments is 11.66 Å. From [4, 5] (see Table 2), the minimum value of c corresponds to an oxygen content of around $O_{6.9}$.

We analyzed the a-axis oriented film by X-ray pole figure determination. This method gives the crystallographic orientation of the crystallites with respect to a specific orientation of the sample. X-ray pole figures were obtained by the Schulz reflection technique [8]. In the {1 0 2/0 1 2} pole figure [7], four poles located at $\phi = 31°$ appear, demonstrating that there are two types of a axis oriented grains, differing by a 90° rotation of the c axis (around the a axis; directions c_1 and c_2). Moreover, from the existence of four poles at $\phi = 56°$, we concluded that part of the film had the c-axis perpendicular to the substrate. Using the calculated intensity of the poles we estimated the volumic proportions to be:

$$c_1 : 44\%, \qquad c_2 : 44\%, \qquad c_\perp : 12\%.$$

Texture was confirmed by HRTEM observations which show grains of 5000–10 000 Å in size made of 100 Å subgrains, corresponding to the directions c_1 and c_2 [7].

Moreover, we have used uniaxial pressure effects along the c axis on a $YBa_2Cu_3O_{7-x}$ twinned single crystal as a reference for the discussion, prepared as described in [9]. The curves of electrical resistance in the (a, b) plane and in the c axis direction exhibit a metallic behaviour with a temperature ratio $\rho(300\,K)/\rho(100\,K) \approx 2$. The anisotropy factor at 300 K between the (a, b) plane and the c axis direction is ≈30. The resistive offset critical temperature T_c is 91.3 ± 0.3 K and the transition width is about 1 K.

2.2. *Cells for resistivity measurements under uniaxial stress*

We designed two cells, sketched on Fig. 1, in which all the parts are in copper–beryllium (Be–Cu), except the pushing disks.

Cell (I) [Fig. 1(a)] allows us to compress bulk samples between two sapphire discs in a cylindrical body. Springs intercalated between the upper pushing disc and the moving piston compensate the differential thermal dilatations. A knee system insures the parallelism of faces. 25 μm diameter Pt electrodes flattened at their extremities can be placed between the sample and the pushing disks to allow four wire measurements.

Cell (II) is used to apply extension or compression stresses to a thin film [position A in Fig. 1(b)] glued on a rectangular flexible Be–Cu plate of 1 mm thickness. Bending the flexible plate by means of a screw extends the film. Compression is possible if we return the support plate. Extension or compression of the film is controlled by a reference strain gauge glued on a piece of the $SrTiO_3$ substrate without deposited film on it, glued itself on the Be–Cu plate.

3. EXPERIMENTAL RESULTS

3.1. c *axis oriented* $YBa_2Cu_3O_{7-x}$ *thin films*

Figure 2(a) shows the resistive transitions of the c axis oriented $YBa_2Cu_3O_{7-x}$ T298 thin film for a cycle of extension stresses up to elongation dl/l of 1280 μm m^{-1}. It can be seen that extension stress shifts T_c towards lower temperatures. The same

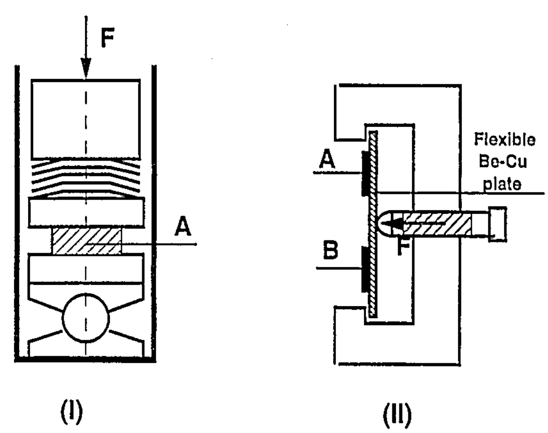

Fig. 1. Uniaxial stress cells: (I) bulk samples, (II) thin films. A is the bulk sample or the thin film, and B is the reference strain gauge.

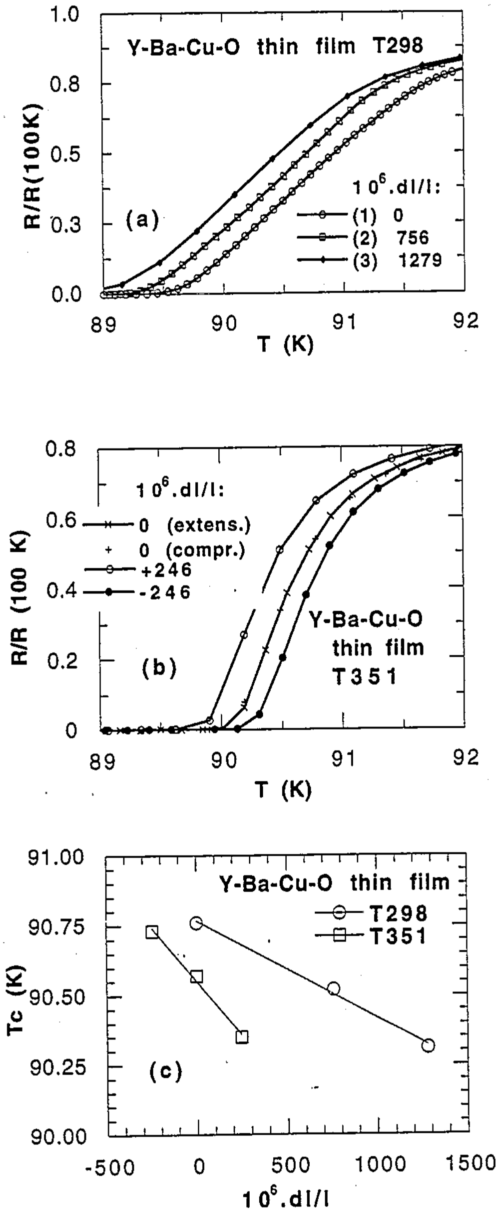

Fig. 2. Thermal dependence of the normalized resistance of c axis oriented thin films for several elongations: (a) T298, (b) T351, (c) variation of T_c of c axis oriented T298 and T351 thin films as a function of elongation.

transition profile is preserved under increasing extension stress. Figure 2(b) displays the resistivity curves of another c axis oriented film (T351) for non-applied pressure, for a stretching $dl/l \approx +246\,\mu m\,m^{-1}$ and for a shortening $dl/l \approx -246\,\mu m\,m^{-1}$. The curves obtained for the Be–Cu support plate in the shortening position ($dl/l = 0$ and $dl/l = -246\,\mu m\,m^{-1}$) were shifted by 0.17 K, the difference observed in the Pt thermometer between stretching and shortening position. We observe that T_c is depressed by stretching, and increased by shortening. The dependence of the superconducting critical temperature under elongation is displayed on Fig. 2(c) for the two samples.

The effect of an uniaxial elongation $\epsilon_{x,x}$ in the (a, b) plane on T_c was determined from the slope of the linear variation of T_c vs dl/l in Fig. 6(c). We found $dT_c/d\epsilon_{xx} = -349$ and -772 K for the T298 and T351 films respectively.

3.2. a *axis oriented* $YBa_2Cu_3O_{7-x}$ *thin films*

Our initial aim was to determine the effect of an uniaxial stress applied along the c axis in $YBa_2Cu_3O_{7-x}$ by applying uniaxial stress to a axis oriented thin films. Unfortunately, these films have two sorts of domains corresponding to two perpendicular directions of c axis: c_1 and c_2 as discussed above. Thus if the stress is applied along c_1, the major effect in the c_2 domains should be a stress in the b axis. Nevertheless some useful information was expected from the experiment: for example, if the pressure effect along c is weak as claimed before, the major effect should come from the c_2 domains and we should find a pressure variation of T_c similar to that found in Section 3.1.

We have thus submitted the a axis oriented $YBa_2Cu_3O_{7-x}$ thin film T450P to cycles of increasing and decreasing uniaxial stresses applied along a c_1 direction. We defined the resistive onset critical temperature $T_{c,\text{on}}$ by the intersection of two straight lines as indicated on Fig. 3(a). Plots of $\Delta T_{c,\text{on}}$ vs dl/l are given on Fig. 3(b) and (c) for two successive cycles. The variation has a serrated aspect: large positive and negative variations occurring successively. This behaviour strongly differs from the c axis oriented $YBa_2Cu_3O_{7-x}$ thin film, and is related to the texture of the film.

We think that this behaviour comes from a weak cohesion between grains and subgrains. Stress is probably transmitted through mechanical contacts between grains and subgrains. The strain endurance limit of such mechanical contacts is probably weak [$\Delta(dl/l) \sim 50\,\mu m\,m^{-1}$ corresponding to a pressure range of $\sim$250 bar]. From the experiment, it seems that extension of the film gives rise to successive overall extension or compression (depending on the mechanical contacts between grains) followed by stress relaxation. Within a range of same stress sign, we calculated a variation of critical temperature of $\approx$20 K kbar^{-1}. This value should be compared to the variation under pressure (19 to 34 K kbar^{-1}) in polycrystalline $YBa_2Cu_3O_7$ [3]. Thus the a axis oriented $YBa_2Cu_3O_{7-x}$ thin films seem to behave as polycrystals as far as the effect of uniaxial stresses is concerned.

3.3. *Twinned single crystal*

Under uniaxial stress applied along the c direction

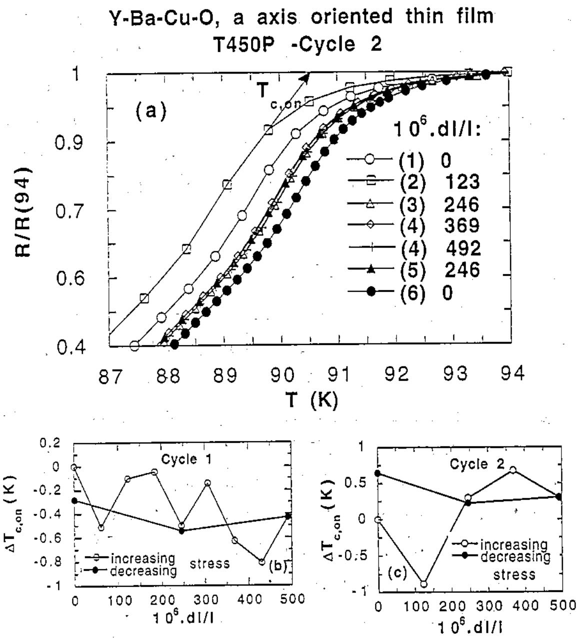

Fig. 3. (a) Thermal dependence of the normalized resistance of an *a* axis oriented thin film for several elongations. Variation of $\Delta T_{c,\text{on}}$ as a function of elongation: (b) cycle 1, (c) cycle 2.

of our single crystal (Fig. 4), we detected no variation of T_c between 0 and 500 bar ($dT_c/d\sigma_c = 0 \pm 0.01\,\text{K kbar}^{-1}$). Above 500 bar, we observed a little decrease of T_c with a broadening of the superconductive transition, probably due to non-uniaxial components of the stress.

4. DISCUSSION

Our experimental results on the $YBa_2Cu_3O_{7-x}$ single crystal indicate a negligible variation of T_c under a uniaxial stress along the *c* axis. Several papers [2, 10] report values of the uniaxial stress dependence of T_c along the *c* axis. They based their calculation on the Ehrenfest relation and used the

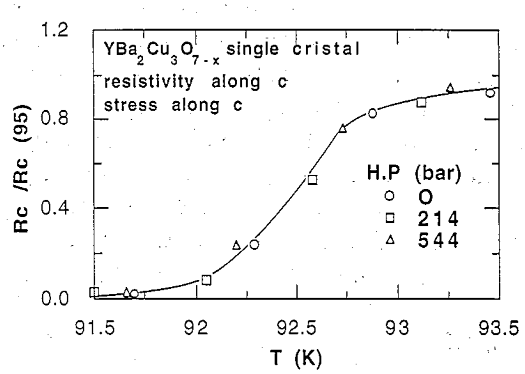

Fig. 4. Thermal dependence of the normalized resistance measured along the *c* axis for several stresses along *c*.

thermal expansion coefficients measured on twinned $YBa_2Cu_3O_{7-x}$ single crystals. The values obtained for $dT_c/d\sigma_c$ are small, respectively $+0.03\,\text{K kbar}^{-1}$ for a single crystal with $T_c = 87.3 \pm 0.65\,\text{K}$ [2] and $-0.027\,\text{K kbar}^{-1}$ for a single crystal with $T_c = 90.8 \pm 0.3\,\text{K}$ (similar to the T_c value of our films) [10]. We have to notice that our determination of the oxygen content is slightly different than in [10] where it is essentially based on T_c whereas in addition we take into account the *c* parameter: we are in agreement with their results if we consider only the T_c value.

The variation of T_c under hydrostatic pressure, dT_c/dp is obtained by summing two contributions:

$$dT_c/dp = 2dT_c/d\sigma_{ab} + dT_c/d\sigma_c. \tag{1}$$

In order to deduce $dT_c/d\sigma_{ab}$ from $dT_c/d\epsilon_x$, we have assumed that in a twinned epitaxied film an elongation ϵ_{xx} in a direction of the *a*, *b* plane induces a stress $\sigma_{ab} \equiv \sigma_{xx} + \sigma_{yy}$. Following [1], the stress along the *ab*-plane can be calculated on the basis of the Hooke's law, using the formula:

$$\sigma_{a,b} = \epsilon_{xx}\frac{(c_{11}+c_{12})c_{33} - 2c_{13}}{c_{33}}. \tag{2}$$

The published experimental values for the components of the elasticity tensor (c_{iklm}) of YBaCuO crystals differ from one author to another one [11–13].

Values of $dT_c/d\sigma_{ab}$, calculated from equation (2), using the elastic coefficients taken from [11–13], are reported in Table 1. In addition, dT_c/dp can also be obtained from equation (1), as $dT_c/d\sigma_c$ is neglected in agreement with measurements on single crystals with a similar T_c. We thus observe a factor of about 2 in the $dT_c/d\sigma_{ab}$ on the two films.

Our results should be compared to those reported in [1], from strain effects on a $YBa_2Cu_3O_7$ twinned *c* axis oriented thin film, obtained by bending the substrate in a cantilever arrangement. They deduced $dT_c/d\sigma_{ab} = 0.045\text{–}0.05\,\text{K kbar}^{-1}$, two times smaller than our values calculated from [13], but for films of lower T_c deposited on a different substrate: MgO (mismatching around 10%) and $LaAlO_3$ (strongly twinned).

Our results of $dT_c/d\epsilon_{xx}$, associated with the elastic coefficients of [13] give values of dT_c/dp in agreement with the previous published effects of hydrostatic pressure on $YBa_2Cu_3O_{7-x}$ bulk ceramics of similar oxygen concentration (Table 2).

We find an experimental large value of $dT_c/d\epsilon_{xx} = -560 \pm 210\,\text{K}$, associated with large $dT_c/d\sigma_{ab}$. This suggests that the pressure effect in this range of doping could come from the variation of the intersite hopping integral *t* which appears in the resonating valence

Table 1. Measured $dT_c/d\epsilon_{xx}$, $dT_c/d\sigma_{ab}$ and dT_c/dp of the films T298 and T351 calculated using the elastic coefficients taken from [11–13]

Thin film	T298	T351
$dT_c/d\epsilon_{xx}$ (K)	−350	−770
$dT_c/d\sigma_{ab}$ (K kbar^{-1})	0.18 [11], 0.24 [12], 0.09 [13]	0.39 [11], 0.53 [12], 0.2 [13]
dT_c/dp (K kbar^{-1})	0.36 [11], 0.48 [12], 0.18 [13]	0.78 [11], 1.06 [12], 0.4 [13]

Table 2. Oxygen content, T_c c and dT_c/dp of $YBa_2Cu_3O_x$

Oxygen content	T_c (K)	c (Å)	dT_c/dp (K kbar^{-1})
Table from [5]			
6.93	92.4		0.04
6.87	90.2		0.25
Table from [4]			
6.98	91	11.686	0.05
6.94	91	11.671	0.05
6.91	91	11.671	0.03
6.87	91	11.671	0.12
6.81	90	11.694	0.28

bond model of Anderson [14] and related models such as the one of Cyrot [15]. Indeed, on the basis of the Anderson model, Griessen [16] expected $d\ln(T_c)/d\ln(V) \approx -2$, leading to $dT_c/dp \approx 0.12\,\mathrm{K\,kbar^{-1}}$ using a bulk modulus of 1500 kbar taken from [13]. This value is similar to that found from the pressure effect measurements on the two thin films investigated here.

Limitations in the precision of uniaxial pressure effects in high T_c superconducting films have essentially two origins which could be connected: oxygen stoichiometry and microstructure. Firstly, we have to recognize that some imprecision lies in the oxygen stoichiometry determined from the value of the c parameter and from electrical transport properties. The microstructure and the gradient of oxygen concentration from the surface to the center of the grains are related and influence the electrical and mechanical properties of the films. It appears that cohesion between grains is insufficient to allow continuous and reversible properties due to uniaxial stress in a axis oriented films.

Another important factor influencing uniaxial stress experiments is the thickness of the films. It is known that there can be elastic matching of deposited growing atomic layers on a substrate when there is a moderate misfit and the thickness of the film is within a critical thickness h_c [17]. In our epitaxied films we did not observe any sizeable broadening of the transition up to a limit of $dl/l = 1.3 \times 10^{-3}$ for the T298 film and only half this limit for the T351 film. Thus we think that h_c is between 900 and 1800 Å. This case could be analogous to Ge_xSi_{1-x} films grown on Si substrates, where h_c is of the order of 1000 Å for a misfit of $\approx 10^{-3}$ [18]. The larger thickness of film T351 may be favourable to the appearance of dislocations under stress inducing larger effects on T_c.

5. CONCLUSIONS

In conclusion we have presented a working method of measuring the effects of uniaxial stresses on thin films grown with different orientations. We determine resistively the dependence of T_c on uniaxial stress in a thin film by bending the substrate.

We confirm that for a single crystal with a T_c around 90 K, the effect of a uniaxial stress along c axis is weak.

For epitaxial a axis oriented thin films we observed relaxation effects of the applied stress, and no intrinsic value for $dT_c/d\sigma_c$ could be determined.

For epitaxial c axis oriented thin films, with a superconducting transition temperature T_c around 90 K, we measured large values of $dT_c/d\epsilon_{xx}$ which differed by a factor of two from one film to the other. This difference can be attributed to the microstructure, the thickness, and the oxygen concentration (the c parameter of T351 is larger than the one of T298). However, these results allow us to calculate the order of magnitude of the hydrostatic pressure effect on T_c (for similar T_c values) using the experimental elastic coefficients of [13]. Moreover, our experiments confirm quite large stress effects in the (a, b) plane, underlining the importance of these effects on the intersite hopping integral as predicted in the RVB type models.

REFERENCES

1. G.L. Belenky, S.M. Green, A. Royburd, C.J. Lobbs, S.J. Hagen & R.L. Greene, *Phys. Rev.* **B44,** 10117 (1991).
2. M. Kund & K. Andres, *Physica* **C205,** 32 (1993).
3. Y. Nishi, N. Ninomiya, K. Oguri & S. Tokunaga, *J. Appl. Phys.* **65,** 3972 (1989).
4. B. Bucher, J. Karpinski, E. Kaldis & P. Wachter, *J. Less-Common Metals* **164&165,** 20 (1990).
5. R. Benischke, T. Weber, W.H. Fietz, J. Metzger, K. Grube, T. Wolf & H. Wühl, *Physica* **C203,** 293 (1992).
6. J.D. Jorgensen, B.W. Veal, A.P. Paulikas, L.J. Nowicki, G.W. Crabtree, H. Claus & W.K. Kwok, *Phys. Rev.* **B41,** 1863 (1990).
7. F. Pourtier-Marty, Doctoral thesis, I.N.P. Grenoble (1994).
8. M. Pernet, D. Chateigner & P. Germi, *J. Alloys and Compounds* **195,** 149 (1993).
9. A. Deville, B. Gaillard, H. Nöel, M. Potel, P. Gougeon & J.C. Levet, *Physica* **C153–155,** 669 (1988).
10. O. Kraut, C. Meingast, G. Bräuchle, H. Claus, A. Erb, G. Müller-Vogt & H. Wühl, *Physica* **C205,** 139 (1993).
11. W. Reichardt, L. Pintschovius, B. Hennion & F. Collin, *Supercond. Sci. Technol.* **1,** 173 (1988).
12. H. Ledbetter & M. Lei, *J. Mater. Res.* **6,** 2253 (1991).
13. H.A. Ludwig, W.H. Fietz & H. Wühl, *Physica* **C197,** 113 (1992).
14. P.W. Anderson, *Science* **235,** 1996 (1987).
15. M. Cyrot, *Solid State Commun.* **62,** 821 (1987).
16. R. Griessen, *Phys. Rev.* **B36,** 5284 (1987).
17. C.A. Ball & J.H. Van der Merwe, *Dislocations in Solids* (Edited by R.N. Nabarro), p. 123. North-Holland, Amsterdam (1983).
18. R. People & J.C. Bean, *Appl. Phys. Lett.* **47,** 322 (1985).