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The Powder Metallurgy of n-Type $Bi_2Te_{2.55}Se_{0.45}$ Thermoelectric Material

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The effects of fabrication by powder processes on the density and thermoelectric properties of an n-type pseudo-binary $Bi_2Te_{2.55}Se_{0.45}$ alloy have been examined. The large effects on the thermoelectric properties are ascribed primarily to the generation and removal of point defects, together with the doping effects of atmospheric contamination in finer powders (−50 mesh).

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1. Introduction

In recent years the effects of the variables of the powder process on the magnetic and electrical properties of materials has become of increasing interest. The relative paucity of information on thermoelectric materials is surprising, in view of the strong dependence of the properties of these materials on the structural defects which largely characterise sintering processes. The information available, apart from the basic study by George and Sharples [1], consists primarily of Russian [2] and German [3] papers, relatively limited in scope. The purpose of the present paper is to report on a wide range of experiments, covering many of the variables involved in fabrication by powder techniques, undertaken for two reasons; firstly to establish an understanding of the basic processes and secondly to determine the relevant control parameters for a production process.

The effectiveness of a material for thermoelectric purposes may be measured by a figure of merit

$$Z = \frac{\alpha^2\sigma}{K}$$

where: α is the Seebeck coefficient; σ the electrical conductivity; K the thermal conductivity.

Owing to the variation of these properties with the density of charge carriers in the material, the figure of merit reaches a maximum value at a charge carrier density of about 10^{19} carriers/cm^3. This maximum value is normally obtained by the addition of doping agents. For the Bi/Te/Se system, the doping material most commonly used for a variety of reasons (uniform distribution, and marginal improvement of figure of merit) is copper bromide.

The size of the n- and p-type blocks currently used in thermoelectric modules is somewhat arbitrary, although the relative dimensions are governed by, among other factors, the operating current and the material parameters. In practice the size of the blocks is of the order of 1 × 1 × 1 cm. Although such blocks can be cut from slabs, it is apparent that the form and size of the blocks suggest the possibility of mass production by powder processes. Because of the anisotropy of the material with respect to the thermoelectric properties, the best materials are oriented single crystals, but highly aligned polycrystalline material is more usually preferred because of its higher mechanical strength. However, over 90% of the maximum figure of merit can be obtained in powder-fabricated samples with a low degree of preferred orientation [4]. For a large number of applications the reduced cost factor greatly outweighs the slight reduction in performance characteristics.

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2. Experimental

The alloys, Bi_2Te_3 with 15 mole % Bi_2Se_3, but with varying levels of copper bromide dope, were prepared by melting the high purity (>99.99%) constituent elements in sealed, evacuated silica tubes. After homogenisation by holding at 800° C, the tubes were oil-quenched to reduce the possibility of segregation during freezing.

After coarse crushing in a jaw crusher, the closest setting of the jaws was used in re-crushing to $-\frac{1}{4}$ in. (−6 mm). Fine grinding was then carried out in a S80 sample mill made by Glen Creston*. This mill uses hardened steel grinding discs in a very small grinding chamber. The size of the mill is 19 × 10 × 20 cm high, and it is thus convenient for use in a protective atmosphere enclosure for atmosphere control.

For the preparation of samples, powder was sieved to obtain either the −18 + 100 mesh, or the −50 mesh fraction.

Two die sizes were used in a floating die body jig to achieve double acting compaction. The smaller size (5 × 6 mm) is the required block size for use in a Peltier heat pump operating at a maximum current of 30 A; the larger (1 × 2 cm) is more convenient for the complete measurement of thermoelectric properties, by the Harman method.

Following sintering, which was carried out in evacuated pyrex tubes, density measurements were made by a displacement method using benzyl alcohol.

Metallographic observations were made by polishing to 0.5 μm diamond paste, followed by etching in bromine and acetic acid or a $2H_2O : 1HCl : 1HNO_3$ mixture.

Measurements of the Seebeck coefficient were made using a 10° C temperature difference at a mean temperature of 294° K. Measurements on small pellets were made by burying the chromel/alumel thermocouples in copper plates attached by surface tension to the samples by an indium/gallium amalgam. It was found that the straight line which could be drawn through points on a plot of voltage difference (chromel/sample/chromel) and temperature difference across the sample, passed through the origin, indicating that no error existed in the measurement of temperature difference because of the amalgam. For the larger blocks, massive copper sheaths round the junctions of the thermocouples with the block were used, eliminating heat transfer along the thermocouples at the measuring junction. This eliminated errors of temperature difference which would otherwise have occurred because of the contact resistance.

Electrical conductivity was measured using an AC four-probe technique. The measurements of room temperature Hall coefficient were made in a field of 8 koe at 80 cycles/sec. The Seebeck coefficients were used in association with the figure of merit measured using the adiabatic resistance [5], to obtain values of the thermal conductivity.

3. Results

3.1. Density

The effects of compacting pressure and powder size on the densities of the as-pressed and as-sintered blocks are shown in fig. 1. It is apparent that above a critical pressure, related to powder size, gas adsorbed or entrapped in compaction expands during the sintering process, thus lowering the sintered density. Further evidence comes from the effects on density of powders compacted after grinding and storing in different atmospheres (fig. 2). The decrease in sintered density with increasing powder storage time is thought to be due to surface adsorption in both cases.

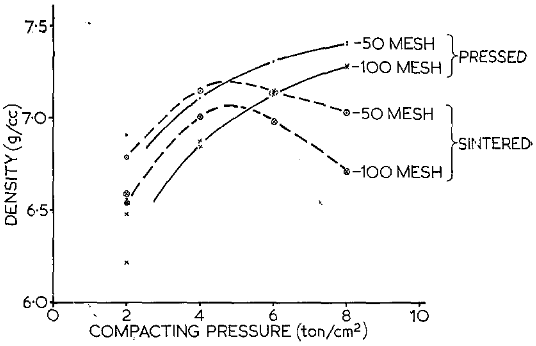

Figure 1 The variation of as-pressed and sintered densities with compacting pressure and grain size of powder. *Note* 1 ton = 1.02 × 10³ kg.

3.2. Sintering Temperature and Time

The effects of sintering temperature on the Seebeck coefficient and electrical conductivities of samples containing different amounts of copper bromide dope are shown in figs. 3 and 4. The behaviour of the conductivity shows a lack of differentiation between the different doping

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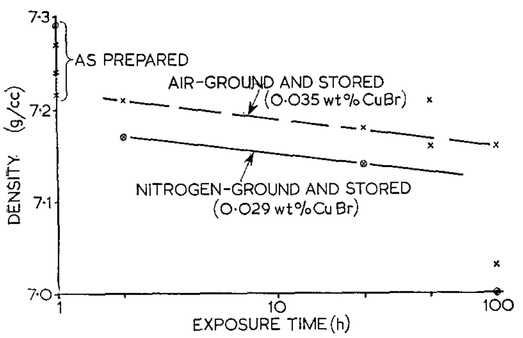

Figure 2 The variation of sintered density with exposure time.

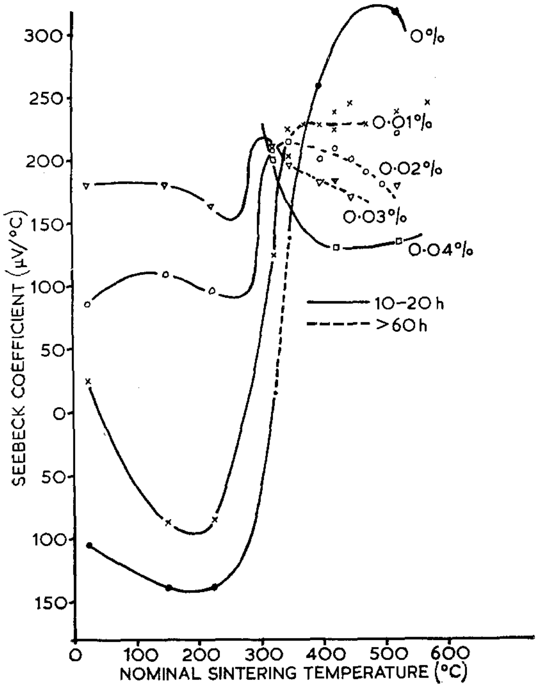

Figure 3 The effect of sintering temperature and CuBr doping level on the Seebeck coefficient.

levels for low sintering temperatures followed by increasing conductivities with increasing sintering temperature, commencing abruptly at 300° C. At high sintering temperatures the conductivities reach different levels, according to the different dope levels. Some of the curves indicate a maximum in conductivity which occurs at lower sintering temperatures with increasing dope levels. The Seebeck coefficient however, particularly at low doping levels, shows a wide range of values over the range of heat treatment temperatures investigated. At the low dope levels, the Seebeck coefficient increases to a maximum for heat treatment temperatures of 200° C, followed by a sharp decrease at higher temperatures. The minimum value occurs at lower treatment temperatures with increasing dope levels. The higher dope levels show a further increase in Seebeck coefficient following this minimum, and comparatively steady values for the heat treatment temperature range 400 to 550° C.

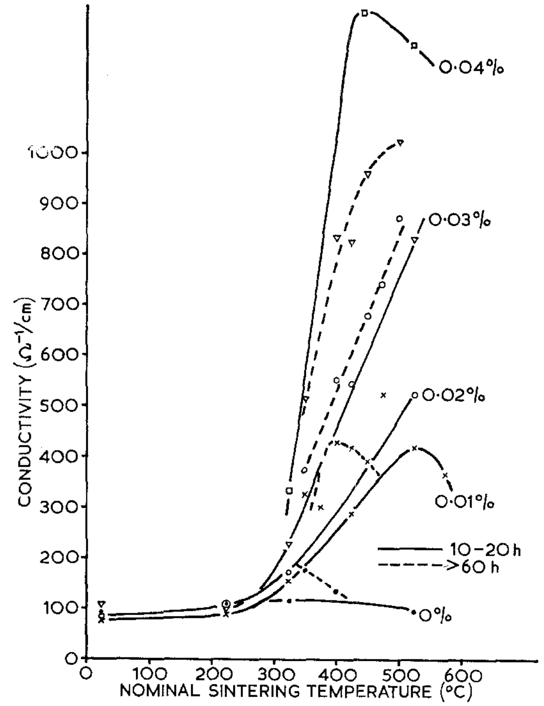

Figure 4 The effect of sintering temperature and CuBr doping level on electrical conductivity.

Over the range of sintering time investigated, both the Seebeck coefficient and the conductivity show effects caused by increasing sintering time, qualitatively similar to those obtained by increased sintering temperatures.

Metallographic observation showed no grain growth during sintering, but recrystallisation within the grains was observed after sintering at 425° C and above.

3.3. Particle Size

Preliminary experiments showed that the effects of particle size on the properties of sintered material were complicated by the effects of surface adsorption. Owing to the lack of facilities for the complete preparation of a range of samples from powders of varying coarseness under fully inert atmospheres, very little work has been done on the effects due solely to particle size. However, work on powders containing coarse particles (up to 18 mesh), in comparison with the same material ground to a finer size in nitrogen, shows an increase in the Seebeck coefficient and a decrease in conductivity with decreasing particle size (table I).

The effects of exposing fine powders to the atmosphere for varying lengths of time on the sintered density have been indicated in fig. 2. This exposure also affects the Seebeck coefficient, and the conductivities of sintered specimens. As the Seebeck coefficient is not sensitive to the degree of porosity of the sample, this property is used to demonstrate the effect of surface contamination. The results shown in fig. 5 show the decrease in Seebeck coefficient of sintered specimens, with increase in time of exposure of the powder to air, and to normal purity nitrogen, before pressing. They also indicate that the effect is more pronounced for the powder ground and stored under nitrogen, indicating the low levels required to produce the effect, and possibly the near-saturation effect produced by grinding in air.

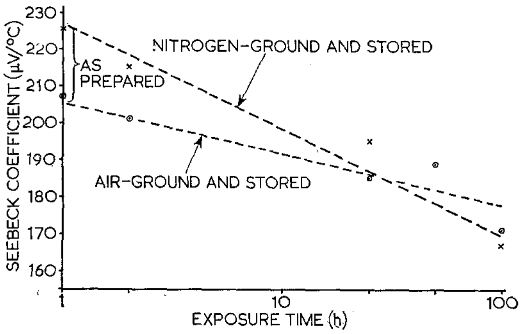

Figure 5 The variation of as-sintered Seebeck coefficient with exposure time of powder. Samples pressed and sintered for 15 h at 500° C.

4. Discussion

The electrical conductivity of a porous material may be written in terms of the bulk conductivity as

$$\sigma_p = \frac{\sigma(2 + \delta)}{2(1 - \delta)} \qquad (1)$$

where δ is the porosity.

In fig. 6 we show that the observed variation of conductivity with porosity, normal to the pressing direction (σ_{11}), is in reasonable accord with predictions based on equation 1. The thermal conductivity exhibits similar behaviour, provided that the pores are not filled with a highly conducting gas and that radiation transport is not important. The ratio of electrical to thermal conductivity is thus, to a first approximation, independent of porosity, and therefore, since the Seebeck coefficient is also independent of porosity, so also is the figure of merit.

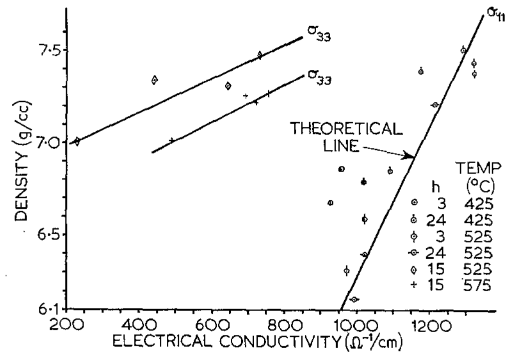

Figure 6 The variation of conductivity with density.

Fig. 6 also shows that the variation with porosity of the conductivity measured in the direction of pressing (σ_{33}) is not in accord with equation 1. The density change on sintering occurs mainly because of dimensional changes in the pressing direction. If we consider the change to be caused by the expansion of trapped gas, which causes isotropic pores surrounded by cracks in the planes of weakness perpendicular to the punch travel, then in the direction parallel to the cracked planes, the normal porosity relations apply, whilst in directions perpendicular to the cracked planes, the conductivity will be greatly reduced. It is apparent that the blocks will be mechanically strongest when the cracking in planes perpendicular to the punch travel is reduced to a minimum; this occurs for maximum density after sintering. Thus for process control it is advisable to work just below the peak density, before cracking in planes starts to occur; thus from fig. 1 a pressure of around 5 ton/cm^2 (1 ton = 1.02 × 10^3 kg) is indicated.

In fig. 7 we show the Seebeck coefficient from fig. 3 as a function of the relevant conductivity taken from fig. 4, measured on the same samples. The form of the curve is the same as that obtained from single-crystal material with varying dope additions, i.e. starting from p-type material, the Seebeck coefficient first decreases

TABLE I Sintered for 15 h at 500° C.

Mesh size	0.035 wt % CuBr, 0.1 wt % Te def.		0.045 wt % CuBr, 0.2 wt % Te def.		0.055 wt % CuBr, 0.3 wt % Te def.	
	$\alpha(\mu V/^\circ C)$	$\sigma(\Omega^{-1}cm^{-1})$	$\alpha(\mu V/^\circ C)$	$\sigma(\Omega^{-1}cm^{-1})$	$\alpha(\mu V/^\circ C)$	$\sigma(\Omega^{-1}cm^{-1})$
18/100 mesh	205	620	234	32	263	221
−50 mesh	231	461	253	282	284	156

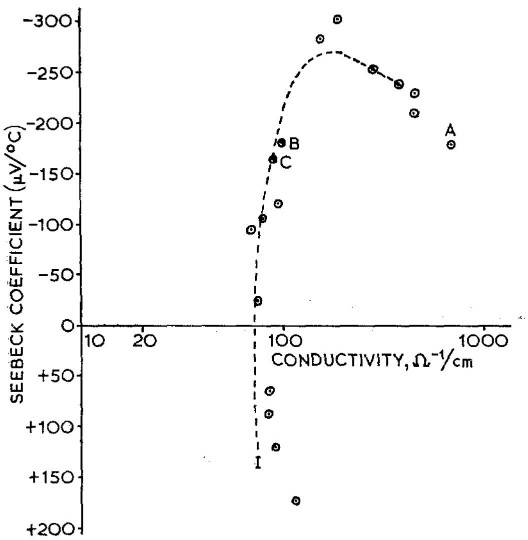

Figure 7 Seebeck coefficient as a function of log conductivity.

rapidly; then, passing through zero, increases with increasing n-type (CuBr) dope additions. Up to this point little change in conductivity occurs; this is the *intrinsic* conduction region. The following region, in which the Seebeck coefficient decreases as the conductivity markedly increases, is termed *extrinsic*. The fact that the effects of heat-treatment shown by our results* follow the same pattern as those obtained on single-crystal material with varying doping levels, indicates that the main processes occur because of changes in the number of free carriers. This is in accord with the results of George *et al* [1], who have shown that changes in the defect concentration in bismuth telluride caused by crushing to powder and pressing followed by sintering, are associated with large changes in the Seebeck coefficient and, by inference, in the carrier concentration. Thus cast and quenched material containing 0.03 wt % copper bromide has properties appropriate to point A (fig. 7). After crushing and pressing, the sample has properties in the intrinsic region (between I and B).

Schultz *et al* [6] estimate that after heavy deformation the number of point defects is of the order of 10^{20} to $10^{21}/cm^3$. Therefore the number of carriers introduced by doping, of the order of $2 \times 10^{19}/cm^3$, is small by comparison; moreover, it is expected that the final state of strain will be roughly constant, and thus that strain introduced because of foreign dope additions to the lattice will result in a smaller number of point defects produced by subsequent deformation. The process is thus to some extent self-compensating. The carrier concentration arising from the point defects, assuming complete ionisation, is the difference between the number of donor centres and the number of acceptor centres. The shift to the intrinsic region described above indicates that this difference is small.

Point B is typical of the results obtained after sintering at about 300° C; different levels of doping cause a limited variation in conductivity (70 to 100 $\Omega^{-1}cm^{-1}$) with an associated larger variation in the Seebeck coefficient.

Annealing below 250° C causes a loss of n-type carriers, resulting in the material moving further towards p-type behaviour, as indicated by point C. Annealing above this temperature results in a larger decrease in p-type carriers and a return of the carrier concentration to its original level. The latter behaviour is in good agreement with the diffusion out of tellurium vacancies postulated by Schultz *et al* [6], and it may be significant that the ratio of the initial absolute heat-treatment temperatures involved in these two processes is close to that of the vacancy activation energies for diffusion of Bi (0.5 eV) and Te (1.09 eV).

The curve of fig. 7 is a function of the energy gap, carrier concentration, and the product of mobility and effective mass ratio, raised to the three halves power, for the n- and p-type carriers. The product for electrons has been obtained

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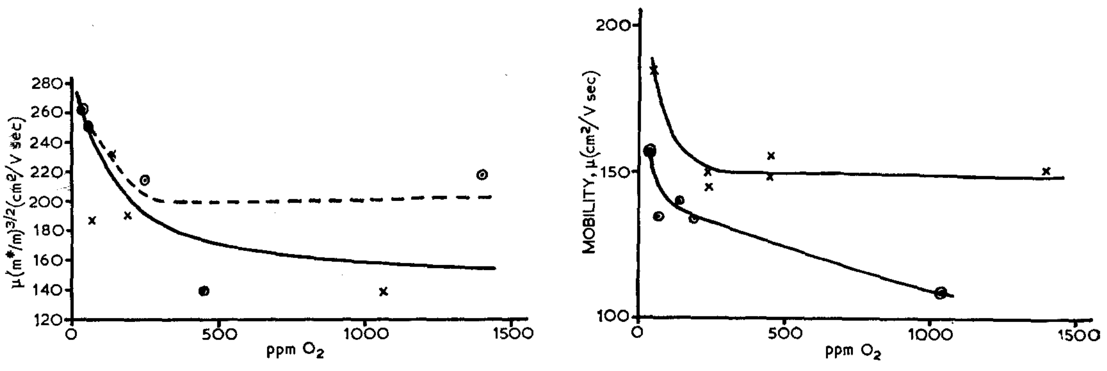
*Since our samples were sintered, the effects of heat-treatment were much more pronounced than in the case of single crystals, whose properties are largely determined by the doping level alone.

from data on extrinsic material, whilst the energy gaps for the 15% Bi_2Se_3 composition is 0.226 eV [7]. Using these data, together with the observed minimum conductivity, we are able to construct, assuming a value for the effective mass of the p-type carriers, a best-fit theoretical curve labelled I. The fit is poor because the conductivity minimum occurs for a positive value of the Seebeck coefficient, which is at variance with the data, as also is the required value of the mobility × effective mass product for holes, which is larger than that for electrons. If this were true then the figure of merit for p-type material would be larger than that for n-type, which is not so. A fit more in accord with observation is possible if it is assumed that the energy gap is of the order of 0.16 eV. Such a supposition is in accord with the large variability of the Seebeck coefficient, attributed to composition variation, observed in cast material by means of a hot probe. Detailed fitting of a theoretical expression is not possible since Hall effect measurements on extrinsic material show that the mobility derived from these measurements increases with increasing time/temperature of heat treatment, as also does the mobility × effective mass product, and thus a theoretical fit to the results in fig. 7 would require variable mobility × effective mass products to allow for the differing heat treatments.

At temperatures above 476° C improvement in the mobility × effective mass product stops after 60 h. The improvement appears to be related to the diffusion out of point defects, and to the observed recrystallisation, rather than to any interaction between grains; this is small, as indicated by the lack of grain growth, and cannot therefore be expected to contribute significantly to any improvement.

Detailed interpretation of the sintering process is made difficult by effects produced by the gas ambient during crushing and/or storage. In this category are the density variations illustrated in fig. 2. These are believed to be produced by the adsorption of gas and/or water vapour on the particle surface which, when heated, is released producing expansion and a lowering of density.

We have established that oxygen interacts with the alloys in the presence of water vapour. Hall effect measurements made on samples in which the concentration was measured by neutron activation analysis [8] show (fig. 8) the sharp drop in mobility and the consequent drop in mobility × effective mass product which occurs with increasing oxygen concentration. These results confirm those of Smirous and Stourac [9] who obtained similar results by the addition of oxygen in the form of Bi_2O_3. Hall measurements further indicate that at concentration levels below 200 ppm, that is before the change in mobility ceases, the oxygen acts as a donor. Storage of powder thus produces material more n-type in character, and if storage is prolonged, inferior, unless air or water vapour are rigorously excluded. In fig. 5 the adsorption doping effect is demonstrated; the difference between the general levels of the Seebeck coefficient is caused by the slightly different materials used in the experiments; the slope is, we believe, caused by an increase in the donor concentration produced by oxygen adsorption. In the case of the air-crushed sample, the slope is less, since the saturation of the doping effect occurs earlier in time.



(a) (b)

Figure 8 (a) Mobility × effective mass as a function of oxygen concentration. (b) Mobility as a function of oxygen concentration.

Decreasing the particle size increases the surface area available for contamination, and thus, unless precautions are taken to exclude air, effects caused by particle size will be obscured. Table I shows results obtained from fine powders ground in nitrogen and pressed immediately. The increase in the Seebeck coefficient is not completely understood. It is suggested that it is associated with the increased surface area, and the consequent larger number of point defects, together with their incomplete removal under the conditions used. The larger number of defects will result in materials closer to intrinsic, as observed.

5. Conclusions

Heat-treatment after crushing and pressing in the bismuth/seleno-telluride system results primarily in the removal of point defects, while homogenisation and recrystallisation increase the mobility × effective mass product. The effects of particle size are associated mainly with increased atmospheric contamination, which at low levels acts as an n-type dope, but at higher levels as a mobility killer. Density variations occur; these are, to a first approximation, of little importance to the thermoelectric properties.

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References

1. W. R. GEORGE, R. SHARPLES, and J. E. THOMPSON, *Proc. Phys. Soc.* **74** (1959) 768.
2. A. N. VORONIN and R. Z. GRINBERG, "Thermoelectric Properties of Semiconductors (Proceedings of the First and Second Conferences on Thermoelectricity)" (Consultants Bureau, New York, 1964) p. 79.
3. F. WENDLER and H. SCHREINER, *Z. Metalk.* **56** (1965) 853.
4. A. W. PENN, to be published.
5. *Idem*, *J. Sci. Instr.* **41** (1964) 626.
6. J. M. SCHULTZ, J. P. MCHUGH, and W. A. TILLER, *J. Appl. Phys.* **33** (1962) 2443.
7. D. L. GREENWAY and G. HARBEKE, *J. Phys. Chem. Solids* **26** (1965) 1585.
8. B. NEBESAR (Bureau of Mines, NRC, Ottawa, Canada), private communication.
9. K. SMIROUS and L. STOURAC, *Czech J. Phys.* **10** (1960) 659.