

changes. On reapproaching the cold-spot, rapid growth should then add new material with properties sufficiently different to cause the observed effects. The wall of crystals seen in Fig. 2 can be explained on a simple geometric basis derived from a careful microscopic examination. The groove cut by the indium is unsymmetrical, with one side much closer in shape to a rectangular cliff than the other, which has a smoother more gradual curve from the bottom of the groove. The rectangular cliff is a more favorable site for the rapid growth of crystals from the indium solution.⁶ The shape of the groove etched by the indium is probably determined by the orientation of "simple" planes, such as the (111), as recently discussed by Moore⁷ for the case of thermal etching of silver. As yet there is no clear evidence on the structure of the crystal in the region of the groove.⁸

R. N. Hall and others⁹ have shown the effect of growth rate on the impurity segregation coefficient and Camp's results show such effects in germanium crystals grown as reported here. However, it does not appear that all of the phenomena noted in the present study can be readily explained solely on the basis of impurity distribution.

The experiments were performed at the General Electric Company in Lynn, Massachusetts with the help of J. B. Seabrook and others.

¹ P. R. Camp, J. Appl. Phys. **25**, 459 (1954).

² A part of this material was reported orally. A. C. English, I.R.E.-A.I.E.E. Conference, Durham, New Hampshire, June, 1951.

³ See for example, H. F. Priest, in *Handbook of Semiconductor Electronics*, edited by L. P. Hunter (McGraw-Hill Book Publishing Company, New York, 1956), Sect. 6.

⁴ The two nonmatching samples are shown since the best contrast for photography is obtained on the two materials at different times.

⁵ J. I. Pankove, R. C. A. Rev. **15**, 75 (1954).

⁶ J. I. Pankove, J. Appl. Phys. **28**, 1054 (1957). In this paper, insufficient recognition is given to the influence of geometry on the delivery of germanium from an indium melt to the growing crystals.

⁷ A. J. W. Moore, Acta Met. **6**, 293 (1958). (See particularly his Fig. 13.)

⁸ A reviewer of this paper comments that he is almost convinced that there are narrow bands of high defect concentration created by the variation of growth rate.

⁹ R. N. Hall, Phys. Rev. **88**, 139 (1952); J. A. Burton, R. C. Prim, and W. P. Slichter, J. Chem. Phys. **21**, 1987-1996 (1953).

cates that gallium antimonide and germanium may be regarded as the components of a simple eutectic pseudobinary system. The eutectic is estimated to occur at 35 ± 10 at. % germanium at a temperature of $648 \pm 4^\circ\text{C}$. The maximum solubility of germanium in gallium antimonide is probably less than 2 at. % under equilibrium conditions.

The procedure by which small amounts of liquid alloys can be quenched rapidly enough to forestall the normal nucleation and growth processes has been previously reported.² A series of alloys was prepared from stoichiometric gallium antimonide ($a = 6.097$ Å) and zone refined germanium ($a = 5.658$ Å). The alloys were cooled rapidly and their resultant structures studied by means of x-ray diffraction. A single phase—with the disordered zincblende structure—was observed in all of the alloys investigated. The plot of lattice parameter vs composition (Fig. 1)³ does not indicate significant or systematic deviation from Vegard's law.

These results were not unexpected. The zincblende structure of gallium antimonide and the diamond structure of germanium are both based upon the necessity of each atom having four nearest neighbors which, in turn, is demanded by the covalent bonding. If the conventional valencies are assigned to the elements, the number of valence electrons/atom remains four throughout the pseudobinary system. Furthermore, the germanium atoms seem to be of such a size as to fit substitutionally into the lattice without causing undue distortion. From a qualitative study of the intensities of the diffraction lines on the Debye-Scherrer films and the absence of any detectable splitting of these lines, it is hypothesized that germanium substitutes randomly in the lattice, and does not destroy the cubic symmetry.

Acknowledgments are made to J. O. McCaldin for providing the alloys and for his continuing interest in this investigation.

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¹ J. O. McCaldin (private communication).

² Pol Duwez, R. H. Willens, and W. Klement, Jr., J. Appl. Phys. **31**, 1136 (1960).

³ The graph of Fig. 1 is based on the nominal composition of the alloys before melting. It has not been possible to obtain reliable chemical analyses thus far. Maximum deviation between nominal and actual compositions might be as large as 5 at. % germanium.

Metastable Solid Solutions in the Gallium Antimonide-Germanium Pseudobinary System*

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THERE seems to be a dearth of published work on the Ga-Sb-Ge ternary system despite the great interest in the semiconductors GaSb and Ge. However, unpublished work¹ indi-

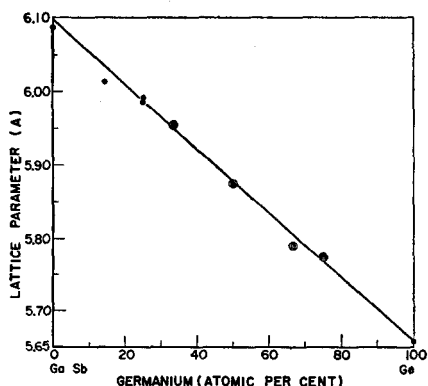


FIG. 1. Lattice parameter vs composition in the germanium-gallium antimonide pseudobinary system.

Anomalous Thermionic Emission from UC and $(\text{ZrC})_{0.8}(\text{UC})_{0.2}$ *

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THE thermionic emission from UC and $(\text{ZrC})_{0.8}(\text{UC})_{0.2}$ solid solution is anomalous in the sense that the parameter A obtained by best fitting the emission data into the Richardson-Dushman equation

$$I = AT^2 \exp(-\phi/kT)$$

is very much larger than A_0 , the theoretical maximum of $120 \text{ amp/cm}^2(\text{°K})^2$ (work function ϕ is assumed constant). Indeed Pidd *et al.*¹ report its value as $7.3 \times 10^6 \text{ amp/cm}^2(\text{°K})^2$ for UC and $6.6 \times 10^4 \text{ amp/cm}^2(\text{°K})^2$ for the $(\text{ZrC})_{0.8}(\text{UC})_{0.2}$ solid solution, when for pure ZrC it is only $134 \text{ amp/cm}^2(\text{°K})^2$. It should be added that previous measurements of the thermionic characteristics of ZrC by Goldwater and Haddad² yielded the value of only $0.3 \text{ amp/cm}^2(\text{°K})^2$ for the coefficient A . The latter authors also reported $A = 3 \times 10^4 \text{ amp/cm}^2(\text{°K})$ for ZrB and $550 \text{ amp/cm}^2(\text{°K})^2$ for ThC; however, they point out that in the latter cases the thermionic emission current never reached steady state. Recently Kmetko³ suggested that such anomalously large emission constants, as well as some anomalously small ones, are due to the relatively large distances between metal atoms in the carbide or boride lattices, as a result of which the energy bands originating from the incomplete atomic f and/or d sublevels are narrow

enough for nondegeneracy to occur in the experimental temperature range.

The purpose of this note is to indicate that the results of Pidd *et al.* also allow another interpretation. Figure 1 represents the

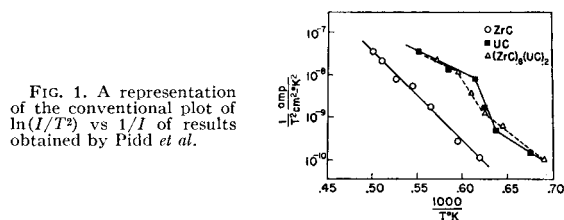


FIG. 1. A representation of the conventional plot of $\ln(I/T^2)$ vs $1/T$ of results obtained by Pidd *et al.*

conventional plot of $\ln(I/T^2)$ vs $1/T$ of the results obtained by them. (In the original paper, $\ln I$ is plotted against $T^\circ\text{K}$.) Whereas the points representing emission current density I from ZrC can be reasonably approximated by one straight line, the ones obtained for UC and $(\text{ZrC})_{0.8}(\text{UC})_{0.2}$ would best be fitted by two straight lines separated by an interval of temperatures $[1590^\circ\text{--}1610^\circ\text{K}$ for UC and $1610^\circ\text{--}1650^\circ\text{K}$ for $(\text{ZrC})_{0.8}(\text{UC})_{0.2}]$ in which rather a sharp increase in current density takes place. It should be emphasized that the above interpretation of these plots may be offered as only a suggestion because of the paucity of data available. The emission data obtained from the plots in Fig. 1 are summarized in Table I.

TABLE I.

Material	Temp. Range	ϕ v	A amp/cm 2 ($^\circ\text{K}$) 2
UC	$T < 1590^\circ\text{K}$	3.62	90.0
	$T > 1610^\circ\text{K}$	2.67	3.5
$(\text{ZrC})_{0.8}(\text{UC})_{0.2}$	$T < 1610^\circ\text{K}$	3.53	55.0
	$T > 1650^\circ\text{K}$	2.53	0.3

In this interpretation the anomaly in A completely disappears. At this point it should be noted that an extremely sharp increase in current density was observed by Pidd *et al.*⁴ when the thermionic current was drawn from a ZrC cathode at Cs vapor pressure of about 2 mm Hg.

The data plotted in Fig. 1 may suggest that the jump in current density in the regions of temperature previously specified is due to some transformation in the cathode materials. As there is no report that the compounds in question undergo any bulk allotropic transformation the only alternative is that the transformation involves the surface atoms.

* This work was performed at the Lockheed Aircraft Corporation Laboratory at Palo Alto, California, to which the author is a consultant.

¹ R. W. Pidd, G. M. Grover, D. J. Roehling, E. W. Salmi, J. D. Farr, N. H. Krikorian, and W. G. Witteman, *J. Appl. Phys.* **30**, 1575 (1959).

² D. C. Goldwater and R. E. Haddad, *J. Appl. Phys.* **22**, 70 (1951).

³ E. A. Kmetko, *Phys. Rev.* **116**, 895 (1959).

⁴ R. W. Pidd, G. M. Grover, E. W. Salmi, D. J. Roehling, and G. F. Erickson, *J. Appl. Phys.* **30**, 1861 (1959).

Dislocation Networks in a Low-Alloy Steel

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PREVIOUSLY, dislocation networks have been observed and studied in some detail in ionic crystals^{1,2} by a decoration technique, and in some fcc metals^{3,4} by the thin-film transmission technique. There is little published information on similar studies in bcc materials. Hirsch,⁵ in a recent review article, showed one picture of such networks due to Venables in strained alpha-iron, whereas Allen⁶ showed one due to McLean in annealed alpha-iron.

It is the purpose of this note to report some recent observations of dislocation networks in a low-alloy steel.



FIG. 1. Square dislocation network. $\sim 80\,000\times$.

The steel used had a nominal composition of 1% Cr, 1% Mn, and 0.4% C. It was first hot rolled to 0.030 in. thick. Subsequent heat treatment consisted of quenching from the austenite region and then tempering at 1250°F (667°C) for 24 hr or at 1325°F (718°C) for 72 hr. To obtain thin sections for electron transmission, the steel was first thinned in orthophosphoric acid to about 0.004 in., then electrolytically polished in a solution of chromic and acetic acid to a thickness of 1000–2000 Å. Observations of the undeformed films were made in a Siemens electron microscope at 100 kv.

The microstructure of the steel (by light micrography) consists of small ferrite grains, either equiaxed or elongated, and carbide particles at the grain boundaries and within the grains. When thin films were examined in the electron microscope, dislocation networks were observed within ferrite grains. Figures 1 and 2 show some typical networks. In Fig. 1 the dark band at the upper right corner is a grain boundary and the black spherical particles are carbides. Several dislocation networks in the form of square grids can be seen. Hexagonal networks were also observed, as shown in Fig. 2. These networks are actually subboundaries which divide



FIG. 2. Hexagonal dislocation network. $\sim 40\,000\times$.

each grain into several subgrains. Frequently they were observed between carbide particles or completely surrounding them. Figures 3 and 4 illustrate these two cases.