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Received 23 January
and accepted 8 February 1976

G. VAN TENDELOO[†]
N. S. MISHRA
C. SURYANARAYANA
Department of Metallurgical Engineering,
Banaras Hindu University,
Varanasi – 221005, India

[†] On leave from Rijksuniversitair Centrum Antwerpen, Middelheimlaan 1, Antwerp, Belgium.

$Nb_6(GaAs)$, $Nb_6(InSb)$ and $Nb_6(GaP)$ new "half-breed" ternary superconductors

While there is, as yet, no basic understanding of the relation of structure or composition to the superconducting transition temperature, empirical search has led to the dominance of two structures: NaCl and β-W, and many compositions involving the element Nb. The discovery that "Nb_3Ge" thin films could be prepared with T_c as high as 22.7 and 23.1 K was a step function advance in this empirical approach. We describe herein a logical extension of this search by the application of elementary crystal chemical principles. The principal aim is to obtain a slight change in band structure of the β-W phase by total elemental substitution. Since the work of Goldschmidt [1] the principle of "half-breeding" to place new elements into a selected structure has been well known. Thus $Si^{4+}O_2$ with the quartz and cristobalite structures can be "half-bred" by replacing Si^{4+} by $(Al^{3+} + As^{5+})$ or $(Ga^{3+} + p^{5+})$ etc. The properties of the resulting $AlAsO_4$ or $GaPO_4$ phases are useful and interesting variants of the properties SiO_2 [2,3]. The whole families of III-V and II-VI semiconductors are, of course, also based on this reasoning (thus [1] p. 144 listed, in 1926, all known useful half-breed III-V and II-V; semiconductors). The present study reports preliminary results on attempting to make [β-tungsten] phases based on Nb_3Ge, with Ge replaced by GaP, AlAs, InSb, and AlSb.

Two approaches were taken to prepare the ternary compounds. The first was an attempt to prepare ingots by solid state reaction at low temperatures. The second was by sputtering onto hot and room temperature substrates. Films deposited on the room temperature substrates were later annealed. For the former, weighed and thoroughly mixed powders were heated in sealed silica tubes for 75h over a range of temperatures. For the r.f. sputtering, the general methods developed in this laboratory [4] were used. Small single crystal sections (roughly 2 cm^2) of the III-V compound were cemented, off-centre, on a niobium target. This permits one to obtain a range of compositions in one run. Although polished polycrystalline Al_2O_3 and silica glass were used in the overall study, the results presented are principally from the films laid down on polycrystalline Al_2O_3. Some twenty films are made in each run. The films so prepared have been analysed routinely with respect to composition on the electron probe, and structure by X-ray diffractometry.

T_c has been measured on the films utilizing a very simple apparatus [5]. In several cases John Gavaler has kindly also measured the samples at the Westinghouse Research Laboratories.

The results of the solid state reacted ingots were immediately of interest, since three obviously isostructural phases were obtained. However, the powder X-ray patterns showed no similarity

TABLE I Powder diffraction data for $Nb_6(InSb)$ in the β-W phase

2θ	d	I/I_0	hkl
30.1	2.969	47	1 1 1
34.1	2.629	80	2 0 0
38.2	2.356	100	2 1 0
42.1	2.146	73	2 1 1
62.4	1.488	47	2 2 2
63.9	1.457	20	3 2 0
66.5	1.406	40	3 2 1
71.75	1.315	20	4 0 0
77.1	1.237	38	4 1 1

Principle diffraction lines for an Nb–In–Sb alloy which was adopted on room temperature substrates and later annealed at 900° C for 3 h. Ni filtered CuKα ($\lambda = 1.5418$ Å) radiation was used in obtaining the diffraction pattern.

TABLE II Superconductivity (onset) transition temperatures

$Nb_6(InSb)$ (hot substrate)	Nb_6InSb (R.T. substrate, annealed)	$Nb_6(GaP)$
6.7	6.0	5.1
7.2	5.8	5.1
7.3	5.9	5.1
7.8	5.7	5.8
	6.0	5.8
	6.4	

The different films should have encompassed any composition gradient in the Nb/III:IV ratio from Nb-saturated down. This appears to be unimportant in affecting T_c.

TABLE III Powder diffraction data

Isostructural ingot/structure unknown						Sputtered film* (β-W structure) ($a_0 = 5.257$)		
$Nb_6(AlAs)$		$Nb_6(AlSb)$		$Nb_6(InSb)$		$Nb_6(InSb)$		
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	hkl
2.857	20	2.984	5	3.675	5	2.969	47	111
2.552	5	2.873	30	2.971	10	2.629	80	200
2.501	20	2.635	10	2.863	30	2.356	100	210
2.440	10	2.556	10	2.711	10	2.146	73	211
2.360	100	2.516	25	2.508	25	1.488	47	222
2.237	10	2.367	100	2.424	10	1.457	20	320
2.203	35	2.335	10	2.367	100	1.406	40	321
2.077	50	2.211	40	2.334	20	1.315	20	400
1.980	15	2.150	25	2.210	40	1.231	38	411
1.601	10	2.084	55	2.086	40			
1.579	10	1.988	15	1.984	15			
1.477	20	1.744	5	1.586	5			
1.470	25	1.603	10	1.556	5			
1.430	20	1.583	10	1.486	30			
1.314	20	1.552	5	1.478	25			
1.220	10	1.490	20	1.440	15			
1.207	15	1.482	25	1.362	15			
		1.475	25	1.269	5			
		1.460	5	1.213	10			
		1.440	15	1.188	5			
		1.406	20	1.169	10			
		1.376	20	1.101	5			
		1.317	5					

*Deposited at room temperature, annealed at 900° C for 3 h.

to β-tungsten or V_3P. The principal diffraction lines are reproduced in Tables I and III.

Films sputtered on the room temperature substrates were largely non-crystalline solids (NCS) with X-ray evidence for a minor amount of very fine Nb crystallites present with the NCS.

When these samples were annealed at 700 to 900° C, or if they were sputtered on to a substrate at 800° C, the InSb samples showed the presence of the ternary analogue $Nb_3(In.Sb.)$ with the β-W structure. Furthermore it was interesting to note that at the lowest annealing temperature, a superstructure with double unit cell was observed, presumably due to ordering of In and Sb. *On the hot substrates only, the disordered* β-tungsten was observed. In the case of GaP, chemical analysis on the electron probe and by X-ray fluorescence, showed that the ratio was approximately Nb_3:1 GaP. In this preliminary study no attempt was made to pin down the elemental ratio precisely.

These ternary composition β-W phases are all superconducting with onset T_c's in the range 5 to 7 K as listed in Table II. These data suffer from the fact that only the onset T_c is recorded, and we have shown elsewhere [6] that the midpoint is more reproducible. Some of the films also show traces of poorly crystallized Nb. The hypothesis has been made [7] that the smallest X atom in the A_3X will help increase T_c. While Nb_3Ge [8] has given the maximum T_c so far, one would expect that there is some reason to hope that T_c in the Nb_6(Ga, P) and a possible $Nb_6(AlP)$ phase would be the highest attainable in the family. A recent paper has reported the formation of Nb_3Si [9] and incidental to the study of the system Nb_3Ga–P, Johnson and Douglass [10] actually report a composition which could correspond roughly to our $Nb_6(GaP)$, although the control of that stoichiometry under the condition used by them would be much more difficult. The Nb_3Si is reported to have a T_c of 9.3 K and the $Nb_3(Ga_{1-x}P_x)$ (notation of Johnson and Douglass [10]) 12 K. It is clear that just as Nb_3Ge was first reported with a much lower T_c, the phases which deserve detailed compositional and structural manipulation are the Nb_3Si and these new half-breed derivatives. Much more detailed work along this line is in process.

Acknowledgements

We are indebted to D. Rogowski for assisting in the sputtering runs and to J. Gavaler for parallel T_c measurements. One of us (V.M.) held an IREX exchange scholarship from the U.S.–USSR program during this period; some support was also received from NSF-MRL Grant DMR74-0034.

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Received 23 January
and accepted 8 February 1976

VALERY MALTSEV
RUSTUM ROY
Materials Research Laboratory,
Pennsylvania State University,
University Park, Pennsylvania,
USA

Thermal stresses in rubber-modified glassy polymers

Thermal stresses that develop in particulate composites during cooling from the fabrication or moulding temperature due to differential thermal contraction of the two phases, can significantly affect strength and toughness of these materials [1–7]. In rubber-modified glassy polymers the thermal expansion coefficient of the rubbery particles is markedly higher than the one of the glassy matrix; when sufficient interphase adhesion is secured, the differential thermal contraction imposes a triaxial tension on the particles and tensile radial and compressive tangential stresses on the surrounding matrix.

According to a mechanism proposed by Schmitt [4], a state of triaxial tension in rubber particles is essential for their toughening action. According to Beck *et al.* [5], the presence of compressive tangential stresses in the matrix surrounding a rubber particle, reducing the maximum local stress produced by an external traction load, contributes to the ductile behaviour of these polyblends. Assuming perfect adhesion between the two phases and neglecting any possible viscoelastic stress relaxation, Beck *et al.* determined the thermal stress distribution for the simple model of a single spherical particle surrounded by an indefinite matrix. On the basis of typical values for the material constants of glassy polymers and rubbers, they also showed the significant order of magnitude of the thermal stresses that can be set up in these composites by ordinary temperature variations. Bohn [7] pointed out that Poisson's ratio of rubbers lies closer to 0.5 than the value taken by Beck *et al.*, and this further raises the level of these thermal stresses.

While the model assumed by Beck *et al.* applies to the case of simple, homogeneous rubber particles included in the glassy matrix, actual rubber-modified glassy polymers, such as toughened polystyrene, ABS, rubber-modified acrylic resins, etc., present a more complex morphology, namely the rubber particles occlude varying amounts of matrix material. The dispersed rubbery phase is thus in itself a particulate composite. In the case of toughened polystyrene the particles may consist prevailingly of polystyrene occlusions surrounded by rubber membranes [8]. To analyse the behaviour of these materials more realistically, the heterogeneous nature of the dispersed phase cannot be disregarded. The aim of this work is a quantitative assessment of the effect of such particle sub-inclusions on thermal stress distribution and magnitude.

In order to take into account the presence of particle subinclusions, one of two methods can be followed: (a) to assume Beck's results for stress distribution but introduce a composite value for the elastic moduli as well as for the thermal expansion coefficient of the composite particle; or (b) to re-model the composite particle. We chose the second way, but followed Beck *et al.* in considering a single particle embedded in an indefinite matrix, assuming perfect adhesion at the interfaces,