

Table 1. Susceptibilities of single crystal and polycrystalline arsenic

Principal mass susceptibilities* of arsenic single crystal				Experimental poly- crystalline arsenic mass susceptibility*		Calculated† polycrystalline mass susceptibility*
T(°K) ±2	$\chi_{\parallel}$ ±0.007	T(°K) ±2	$\chi_{\perp}$ ±0.005	T(°K) ±2	$\chi$ poly- ±0.003	$1/3\chi_{\parallel}+2/3\chi_{\perp}$ ±0.006
82	+1.005	82	-0.238	84	+0.146	
129	+0.891	120	-0.252	84	+0.146	
194	+0.765	180	-0.262	84	+0.148	+0.171
230	+0.687	239	-0.274	150	+0.111	+0.113
246	+0.654	291	-0.281	151	+0.110	+0.111
292	+0.578	292	-0.279	179	+0.094	+0.087
311	+0.547	362	-0.289	181	+0.092	+0.085
354	+0.479	433	-0.302	233	+0.061	+0.043
391	+0.435	458	-0.302	297	+0.015	+0.001
428	+0.375	510	-0.302	298	+0.016	+0.001
472	+0.321	540	-0.303	364	-0.034	-0.041
496	+0.297			426	-0.070	-0.073
531	+0.273			442	-0.078	-0.080
				461	-0.087	-0.089

\* C.g.s. e.m.u./g.10<sup>6</sup>, extrapolated to infinite field strength.

† A smooth curve was drawn through  $\chi_{\parallel}$  and  $\chi_{\perp}$  vs. temperature, and the quantity  $1/3\chi_{\parallel}+2/3\chi_{\perp}$  calculated at those temperatures for which susceptibilities were determined for polycrystalline arsenic.

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### Properties of the residual acceptors in GaSb from reactions with Li\*

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RECENTLY BAXTER *et al.*<sup>(1-3)</sup> concluded from electrical measurements on Li-doped GaSb that the residual acceptor A, normally found in pure GaSb, should be a double acceptor, probably a Ga atom on an Sb site, and that ion-pairing between A and Li, to form (A·Li) single acceptors, occurred. From our investigations of the behaviour of Li in GaSb we reached a different conclusion on the nature of A.

GaSb single crystals were grown by Czochralski's method. Li was introduced in the crystals

from a dispersion of Li in mineral oil. The solubility and diffusivity were investigated as a function of temperature by electrical and flame-photometrical analyses.†

The following results could be related to the residual acceptors.

1. The limiting saturation solubility of Li at temperatures below about 625°K, and measured down to 550°K, proved to be three times that of the concentration of free holes found in our GaSb, for core as well as for non-core material.<sup>(4)</sup> At temperatures above 625°K, where the solubility was a function of temperature, a difference in solubility between core and non-core material was also found. This difference in solubility could be determined at three times the difference between the number of free holes for core and non-core GaSb. Above 800°K, where the solubility exceeded  $3 \times 10^{18}$  Li atoms cm<sup>-3</sup>, we could no longer detect this difference because the accuracy of the flame-photometric analysis amounts to only 10% of the total Li content.

\* This work was part of a thesis submitted at the University of Utrecht, 1965.

† Detailed results concerning Li in GaSb will be published elsewhere.

2. Independently of the diffusion temperature, the introduction of up to  $2[A]$  Li atoms,  $[A]$  being the concentration of free holes originally present, did not result in any change of the resistivity, whereas  $3[A]$  Li atoms resulted in a complete compensation of current carriers.

3. For a concentration of Li larger than  $2[A]$  the residual acceptor level was destroyed completely. A new acceptor level was found, having an ionization energy of about  $10^{-2}$  eV.

4. At room temperature the Hall mobility,  $\mu_H$ , of GaSb containing Li was in general the same or only slightly decreased, relative to that for pure GaSb. At lower temperatures  $\mu_H$  for pure GaSb was larger.

Assuming that the defect A is a Ga vacancy most of our results can be explained rather well. We start from the basic ideas of Fuller and Wolfstirn about incorporation of Li in GaAs,<sup>(5,6)</sup> A reaction between Li atoms and a Ga vacancy results in the associate  $(Li_{Ga}Li)_A$ . Vacancies and associates are assumed to be single acceptors; furthermore we assume that one Li atom on a Ga site is unstable. The introduction of 2 Li atoms for each A originally present will not therefore change the room temperature resistivity at all, because each single acceptor A is replaced by one single acceptor  $(Li_{Ga}Li)_A$  and both acceptors are fully ionized at room temperature. The new acceptor  $(Li_{Ga}Li)_A$  will give rise to an increased solubility of interstitial Li donors to the same amount as there are  $(Li_{Ga}Li)_A$  acceptors, resulting in a complete compensation of current carriers at a total Li concentration  $3[A]$ . That only an equal number of Li donors has been introduced and that no further reaction has occurred to form the neutral associate  $(Li_{Ga}Li_2)_A$  at a comparably large concentration level, may be deduced from  $\mu_H$  found in this concentration range. If the enhanced resistivity were caused by association we would expect an increase of  $\mu_H$ , due to the decreased number of charged scattering centres.<sup>(7)</sup> We generally found a slight decrease, however, which is indeed expected when no further association takes place, because the number of charged scattering centres has then been doubled.

Our results cannot be explained with the double acceptor model as suggested by BAXTER *et al.* In that case one would not expect a maximum in resistivity at  $3[A]$  and an unchanged resistivity

below  $2[A]$ . One would expect a continuous increase in resistivity as a function of the amount of Li introduced, i.e. one free hole being captured for each Li atom introduced. Furthermore the maximum in resistivity should be found at a Li concentration of  $2[A]$ .

There remains one difficulty, however. We have found that rather high amounts of Li (up to  $4 \times 10^{19}$  atoms/cm<sup>3</sup>) could be introduced at higher temperatures in a relatively short time. The incorporation model of Fuller and Wolfstirn, which we also assume with some modifications, requires a relatively fast diffusion of Ga vacancies. However, this appeared to be in contradiction to the compensation found, even after the highest temperature diffusion experiments, at a Li concentration  $3[A]$ . On the assumption that defect A is a Ga vacancy, there would be no reason why the defects A, if they were present at too high a non-equilibrium value, should not diffuse out of the crystal, or why, if they were present at their equilibrium concentration, a reaction of defects A with Li should not result in the introduction of fresh defects A into the lattice. In both cases no compensation is to be expected at  $3[A]$  at all.

The experimental data that GaSb grown from Sb-rich melts shows a higher resistivity than crystals grown from equimolecular melts,<sup>(8)</sup> can be explained most straightforwardly by assuming that the residual acceptor is a Ga atom on an Sb site. This model cannot explain our experimental results, as was shown above. One can only conclude that the defect A must be more complex. It may be an associated form of the two single defects treated above: a gallium vacancy coupled with a gallium atom on an antimony site.

We have to make one final remark. As a consequence of the accuracy of the flame-photometric analyses our experiments do not exclude completely the possible presence of other defects with acceptor behaviour. However, for a simple single acceptor impurity the concentration has to be lower than  $4 \times 10^{16}$  cm<sup>-3</sup>.

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### Thermoelectric power in niobium-zirconium alloys†

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THE thermoelectric power of niobium is known to exhibit a relatively large positive peak at  $T \approx 80^\circ\text{K}$ .<sup>(1)</sup> Assuming the presence of a phonon drag component<sup>(2)</sup> one can anticipate a change in the magnitude of this peak when sufficient amounts of zirconium are added to niobium. Information regarding the transport properties of simpler metals has been obtained by observing quenching of the phonon drag peak in copper based alloys.<sup>(3,4)</sup> In addition, one expects a variation in diffusion

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thermopower with alloying. Hence, to obtain information regarding the relatively unexplored transport properties of Nb-Zr alloys, we have determined the thermoelectric power of niobium and several Nb-Zr alloys from  $T = 9.2$  to  $330^\circ\text{K}$ . Since the original niobium data extends only to the low temperature limit of  $14^\circ\text{K}$ , the current results constitute an extension to lower temperatures of previously published results.<sup>(1)</sup>

Measurements were carried out on niobium and Nb-Zr alloys containing 1, 1.8 and 3.8 at. % zirconium as determined by spectrochemical analysis. The finished material in the form of 0.010 in. D wire was supplied by the Materials Research Corporation, using their high purity zone refined stock as starting materials.<sup>(5)</sup> After working, both Nb and the alloys were annealed for four hours at  $1000^\circ\text{C}$  in a dynamic vacuum of  $7 \times 10^{-6}$  torr. For the annealed niobium, the ratio between resistivities measured at  $295$  and  $10^\circ\text{K}$  was 28. The major impurities in the niobium sample, as determined by spectrochemical analysis were, Ta (500 ppm), Mo (100 ppm) and oxygen (52 ppm). In obtaining the thermoelectric power, either the niobium or alloy samples was clamped in a copper holder to which a copper wire had been soldered. This constituted the hot junction of a thermocouple which was placed in good thermal contact with a heater contained in a vacuum chamber. The reference junction of this thermocouple was kept at either liquid helium or liquid nitrogen temperatures. Pressures as low as  $10^{-5}$  torr were maintained in this assembly which was immersed in either liquid helium or liquid nitrogen, depending on the temperature range to be covered. Thermal e.m.f.'s generated by the couple were determined by means of a Rubicon "thermo-free" potentiometer. Temperatures below  $77^\circ\text{K}$  were determined with a germanium resistance thermometer while a copper-constantan thermocouple was used for the higher range of temperatures. Thermoelectric powers were obtained by differentiating the e.m.f. vs. temp. data using a computer program based on the method outlined by HENRY and SCHROEDER.<sup>(6)</sup> The absolute thermopower of Nb and the alloys were obtained after calibrating the copper wire and holder against high purity lead.<sup>(7)</sup> The thermopower results are shown in Fig. 1, where, to minimize confusion, data points are shown only for the 3.8% alloy.