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Abstract

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ON THE DISSOLUTION OF GERMANIUM IN CERTAIN TERNARY SEMICONDUCTOR COMPOUNDS

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The question of the solubility of germanium in semiconductor compounds with a diamond-like structure attracts the attention of researchers for at least two reasons. First, it is important to determine the possibility of doping a number of semiconductors with germanium. Second, the question of the dissolution of germanium in semiconductors in macroquantities is of interest from the standpoint of the possibility of creating alloys with intermediate properties.

As is known, the position of germanium in the periodic system determines the duality in the behavior of some of its compounds, which exhibit amphoteric properties. The amphoteric character of germanium is manifested, for example, also in the fact that, being a component of semiconductor compounds, it can occupy both "anion" and "cation" positions in the crystal lattices of the corresponding substances (for example, in Mg_2Ge, GeTe).

In studying the behavior of germanium as a dopant impurity in gallium arsenide, it was found that germanium, dissolving in small amounts (up to 0.5 at.%), creates donor or acceptor levels in gallium arsenide (depending on the method of preparing the arsenide), substituting either for positions of gallium atoms or for those of arsenic atoms (1). Moreover, in investigating the electrical properties of germanium-doped arsenide, the authors of work (2) come to the conclusion that part of the dissolved germanium atoms simultaneously occupy both "cation" and "anion" positions in the lattice.

All this suggests that germanium may dissolve in semiconductor compounds in quantities considerably larger than has been observed up to now. However, attempts to dissolve any substantial amounts of germanium in compounds of the type A^3B^5 led to negative results, which Folberth (3) interpreted as a result of the excessively large difference in the type of chemical bond between A^3B^5 and A^4.

Having analyzed all the data, we assumed that the effect of dissolving macroquantities of germanium could be achieved by choosing, as solvent, a compound still closer to it in type of chemical bond than the A^3B^5 compounds studied so far. Ternary compounds of the type $A^2B^4C^5_2$, as the first results of their

Diffraction-line diagrams for $ZnGeAs_2$ and solid solutions: No. 1 $ZnGeAs_2$; No. 2 94% $ZnGeAs_2 \cdot 6\%4Ge$; No. 3 90% $ZnGeAs_2 \cdot 10\%(4Ge)$.

Figure 1: Diffraction-line diagrams for $ZnGeAs_2$ and solid solutions: No. 1 $ZnGeAs_2$; No. 2 94% $ZnGeAs_2 \cdot 6\%4Ge$; No. 3 90% $ZnGeAs_2 \cdot 10\%(4Ge)$.

investigation in our laboratory have shown, apparently are, in type of chemical bond, intermediate between their crystallochemical analogues A^4 and A^3B^5 (^{4}).

At the same time, our earlier observations of isomorphous heterovalent substitutions showed that they are very characteristic of the germanium series (for example, (^{5})). Therefore, the compound $ZnGeAs_2$, an isoelectronic analogue of germanium, was chosen as the solvent for germanium.

The second type of ternary compounds in which we also assume a type of bond close to that in A^4 is the type $A^1B^4_2C^5_3$. Unfortunately, in this type only two compounds crystallize in a diamond-like structure: $CuSi_2P_3$ and $CuGe_2P_3$. The compound of this type closest to germanium in composition, $CuGe_2P_3$, also served as an object for studying the solubility of germanium in it.

The synthesis of samples of the Zn—Ge—As system along the $ZnGeAs_2$—4Ge section was carried out by the usual melting method, widely known in the literature. The samples were obtained in the form of dense ingots, for the most part coarse-crystalline. Thirteen alloys were studied. The investigation showed that solid solutions form over a wide concentration range. Under normal cooling (at a rate of 100–150° per hour), the compound $ZnGeAs_2$ crystallizes in the chalcopyrite structure with parameters $a = 5.660$ kX and $c = 11.136$ kX. Figure 1 presents the diffraction-line diagrams of the compound $ZnGeAs_2$ and of solid solutions of compositions 94 mol.% $ZnGeAs_2 \cdot 6\%(4Ge)$ and 90 mol.% $ZnGeAs_2 \cdot 10\%(4Ge)$.

Fig. 1

On microsections of the compound (and subsequently of solid solutions of this compound with germanium) obtained in this way, the presence of a small amount (2-3%) of a second phase was always observed; this phase disappeared completely when the samples were synthesized using directional crystallization.

Alloys of $ZnGeAs_2$ with germanium retain the chalcopyrite structure up to alloys of composition 92% $ZnGeAs_2 \cdot 8(4Ge)$. All alloys with a higher germanium content have the zinc-blende structure, and their parameter varies linearly with composition from $a = 5.6340 \pm 0.0005$ kX for the composition $ZnGeAs_2$ (on quenching) to $a = 5.6389 \pm 0.0005$ kX for the composition $2ZnGeAs_2 \cdot 4Ge$. At a germanium content of 25 mol.% and higher, on polished sections of the alloys there appears

second phase. Identification of the second phase on Debyegrams proves difficult because of the closeness of the parameters.

Fig. 2

Figure 2: Fig. 2

Examination of microsections showed that alloys in this composition region (more than 33.3 mol.% Ge) have two structural constituents: primary crystals and a finely dispersed mixture. Up to the composition with 55 mol.% germanium, the amount of the finely dispersed mixture increases with increasing germanium content, and after this composition it gradually decreases. The alloy of composition 45 mol.% $ZnGeAs_2$ + 55 mol.% (4Ge), which has the appearance of a uniform mixture of two phases, is apparently eutectic. Figure 2 presents the phase diagram of the system obtained by thermal-analysis method.

Fig. 2

According to microstructural analysis, the solid solutions extend up to 25 mol.% germanium.

In the region corresponding to the formation of substitutional solid solutions, the alloys can be obtained as strictly single-phase, as in the case of the compound $ZnGeAs_2$, by synthesis using directed crystallization.

In the Cu–Ge–P system, the section $CuGe_2P_3$–6Ge was investigated by fusing the components in a two-temperature furnace. The compound $CuGe_2P_3$, discovered by us (^{6}), and then by Folbert et al. in 1960 (^{7}), crystallizes in the zinc-blende structure with parameter $a = 5.38$ kX. As in the preceding case, $CuGe_2P_3$ alloys could be made strictly single-phase only by using special techniques. Alloys of this compound with different germanium contents (10 alloys were investigated) up to the composition $CuGe_2P_3 \cdot (3Ge)$ were single-phase and gave one system of lines on the Debyegram. The lattice period varied linearly with composition from $a = 5.38$ kX to $a = 5.48$ kX. With increasing germanium content, additional lines appeared on the Debyegrams of the alloys.

Earlier we undertook attempts to elucidate the mechanism of germanium dissolution in the compound $CuGe_2P_3$ (^{8}). This question was studied by the X-ray structural method of intensity analysis. The authors came to the conclusion that, upon dissolution, germanium atoms occupy both cationic and anionic sites simultaneously. By the method described in (^{8}), an intensity analysis was also carried out for alloys of the section $ZnGeAs_2 \cdot (4Ge)$. The results obtained are completely analogous to the preceding ones, i.e., it was shown that germanium atoms replace in $ZnGeAs_2$ both zinc atoms and arsenic atoms.

In addition to the two substances mentioned, in order to determine the prevalence

To this end, several more alloys based on diamond-like ternary compounds and germanium were synthesized.

Preliminary experiments showed that germanium dissolves in appreciable amounts (~14 mol.%) in Cu_2GeSe_3 and in some other ternary and more complex compounds containing germanium, but not in all of them.

Thus, the dissolution of germanium in its complex crystal-chemical analogues may be regarded as an established fact. It is probable that, in order to obtain an understanding of the conditions necessary for the dissolution of large amounts of germanium in a given compound, a considerably wider range of substances must be studied, which we regard as our further task.

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REFERENCES

1. R. Solomon, J. Electrochem. Soc., **108**, 7 (1961).
2. C. Kolm, S. A. Kulin, B. L. Averbach, Phys. Rev., **108**, 4 (1957).
3. O. G. Folberth, H. Welker, J. Phys. Chem. Sol., **8**, 14 (1959).
4. N. A. Goryunova, S. Mamaev, V. D. Prochukhan, DAN, **142**, No. 3, 623 (1962).
5. N. A. Goryunova, V. S. Grigorieva, ZhTF, **26**, 10 (1956).
6. N. A. Goryunova, V. I. Sokolova, Izv. Mold. Branch, Academy of Sciences of the USSR, **3**, 69, 1961.
7. O. G. Folberth, H. Pfister, Acta crystallogr., **14**, 325 (1961).
8. N. A. Goryunova, A. A. Vaipolin, Tszyan Bin-Si, Fizika i khimiya, Reports at the XIX Scientific Conference, 27, 1961, Leningrad.

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