Instabilities In Atomic Positions – A Way For Increasing The Thermoelectric Figure Of Merit

M.I.Fedorov, L.V.Prokof'eva, V.K.Zaitsev

A.F.Ioffe Physico-technical Institute of the Russian Academy of Sciences,
194021, Polytekhnicheskaya ul., 26, St.Petersburg, Russia

Abstract

It is clear that the conception of PGEC (Phonon Glass Electcronic Crystal) shows a goal in the thermoelectric material science. Really, if the thermal conductivity of some kind of glass is estimated as 0.1 $W{\cdot}m^{-1}K^{-1}$, and the power factor of a thermoelectric alloy achieves 0.01 $W{\cdot}m^{-1}K^{-2}$, even at room temperature we receive ZT=30, and, hence, the coefficient of performance of a thermoelectric generator becomes practically equal to that of Carnot cycle. In this splendid prospect there is only one black mark. It is the question: "How to do it?" And this black mark becomes much more important than the mentioned splendid prospect.

In this paper we shall try to discuss some ways of increasing the figure of merit. These ways are PGEC conception and mobility edge conception. We shall discuss the possibility of materials with so-called "instable" atom positions for energy conversion. What do we understand as the crystal lattice with "instable" atom positions? It is a crystal where weak action could significantly change atomic positions. For example, crystal structure can be changed in higher manganese silicide when slight changing Mn/Si ratio. It could lead to an energy barrier system creation and additional scattering of current carriers of low energy. Another variant takes place in solid solutions $PbTe_{1-2x}Se_xS_x$, where impurity atom (S) can easy change its position, although the main lattice is a stable one. This leads to additional scattering of phonons. There are other materials with "instable" lattice.

Experimental and theoretical results on the study of thermoelectric properties of some silicides and PbTe-based solid solutions are discussed in the framework of the conception of materials with "instable" lattice. It is shown that the use of such materials can be a way for increasing the thermoelectric figure of merit.

Introduction.

There are two main ways of increasing thermoelectric figure of merit. The first of them is changing the properties of phonon system without significant influence on the current carrier system. The solid solution method was the first variant of this way [1]. The limit of this method is the PGEC conception – Phonon Glass Electronic Crystal [2]. The second way is to change current carrier system to increase density of states at Fermi level without shifting its position relatively conduction or valence band extremum. It will allow to increase power factor significantly without increasing thermal conductivity. There are two limit variants of this way: a mobility edge [3, 4] and quantum well structure [5]. The only disadvantage of these ways is that they do not show how to reach these limits. In this paper we shall discuss the possible variants how one can move in the direction of these limits.

PGEC conception.

It is clear that the conception of PGEC shows a goal in the thermoelectric material science. Really, if the thermal conductivity of some kind of glass is estimated as 0.1 $W{\cdot}m^{-1}K^{-1}$, and the power factor of a thermoelectric alloy achieves 0.01 $W{\cdot}m^{-1}K^{-2}$, even at room temperature we receive ZT=30, and, hence, the coefficient of performance of a thermoelectric generator becomes practically equal to that of Carnot cycle. In this splendid prospect there is only one black mark. It is the question: "How to do it?" And this black mark becomes much more important than the mentioned splendid prospect. The most known way of PGEC conception realization is the idea applied in filled skutterudites. In these materials a void in crystal structure can be filled by a heavy atom. In ideal case if the void is filled by a neutral atom (having no bonds with other atoms), this atom increases significantly phonon scattering and its influence on electronic system is not so essential. Really, we have not a neutral atom in the void, but some of its electrons participate in forming new bonds with neighbouring atoms and its insertion changes the electron system very strongly [4].

A question arises, how to insert a scattering center for phonons into a crystal lattice. There is a good idea. Sometimes in a material there are few places where a guest atom can be placed to. If the energy necessary to change the positions is not too high, it can be received from phonon subsystem. In this case such a guest atom could be an additional scattering center for phonons and it would influence on electron subsystem less strongly. One of such materials could be a $Pb_{1-2x}Se_xS_xTe$ solid solution.

$Pb_{1-2x}(SeS)_xTe$ solid solutions

In the solid solutions $PbTe_{1-x}S_x$ sulphur atoms takes off-center positions. It has been revealed using a direct method of X-ray absorption fine-structure spectroscopy [5]. There are several alternative off-center positions for impurities, with possible tunneling between them.

In this case the sulphur atoms have to give additional contribution in thermal resistance of the crystal lattice in comparison, for example, with selenium atoms. The difficulty is that sulphur and tellurium have higher mass difference than selenium and tellurium and, hense, sulphur has to decrease thermal conductivity more effectively than selenium. Let's see a figure 1 showing the thermal resistance of crystal lattice for some PbTe-based solid solutions. Lattice thermal resistance was calculated in a usual way using Wiedemann-Franz law from the results of measurements of total thermal conductivity of undoped samples. One can see that addition of sulphur increases thermal resistance much stronger than addition of selenium. Moreover, joint addition of S and Se gives additional contribution in thermal resistance. Usually the thermal resistance of the solid solution

$A_{1-2x}B_xC_x$ has to be a half of the sum of thermal resistances of $A_{1-2x}B_{2x}$ and $A_{1-2x}C_{2x}$ solid solutions. In this case the thermal resistance of $PbTe_{0.9}Se_{0.05}S_{0.05}$ is practically the same as that of $PbTe_{0.9}S_{0.1}$, but the mobility of current carriers in the former solid solution is about twice higher than that in the latter [6].

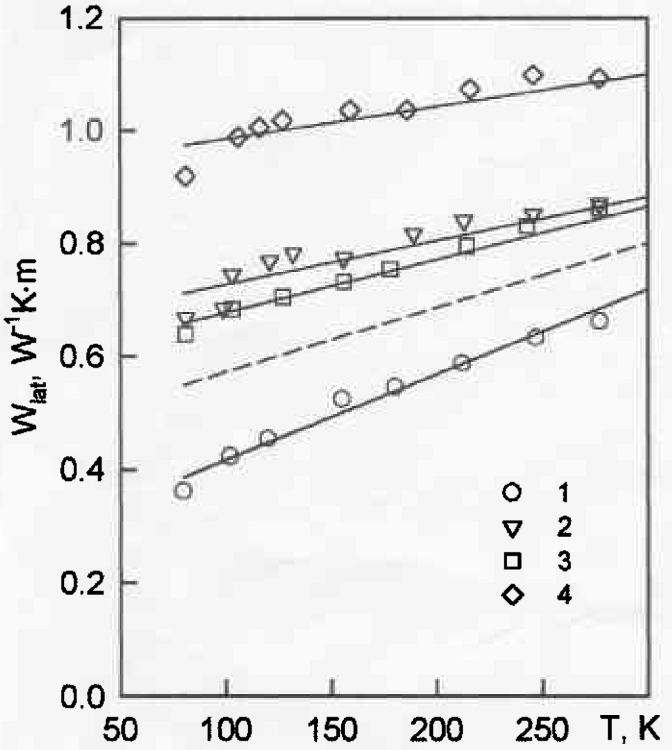

Figure 1. Thermal resistance of $PbTe_{1-x-y}Se_xS_y$ solid solutions. 1 - x=0.1, y=0; 2 - x=0, y=0.1; 3 - x=y=0.05; 4 - x=y=0.1. Dashed line shows the dependence $(W_1+W_2)/2$.

Let us see how sulphur impurity influences on electron subsystem. As a result of off-center positions of S atoms, tunneling states are formed with closely spaced energy levels. These tunneling states have specific properties; in particular, they scatter carriers similarly to impurities responsible for the Kondo effect. In the Kondo effect, the resistivity increases logarithmically as the temperature decreases. Another effect related to the off-center position of an impurity is the formation of a random dipole structure [6]. The random dipole structure can provoke even stronger low-temperature carrier scattering than the Kondo effect.

Figures 2 and 3 shows electrical conductivity of undoped samples of $PbTe_{1-x-y}Se_xS_y$ solid solutions. One can see that both doped and undoped samples containing not less than 10% PbS have unusual temperature dependencies of electrical conductivity. So, one can conclude that the influence of off-center positions of impurity influence strongly on both phonon and electron subsystems.

Seebeck coefficient of the solid solutions under discussion is practically the same for the sample of low current carrier concentration. So, the joint addition of selenium and sulphur allows to increase the figure of merit of these materials at low temperatures. Figure 4 shows a set of curves for figure of merit of some of mentioned materials. One can see that the solid solutions $PbTe_{1-x-y}Se_xS_y$ have higher figure of merit than $PbTe_{1-x}Se_x$ solid solutions, but the figure of merit decrease when temperature decreasing for the former material is stronger than that for the latter.

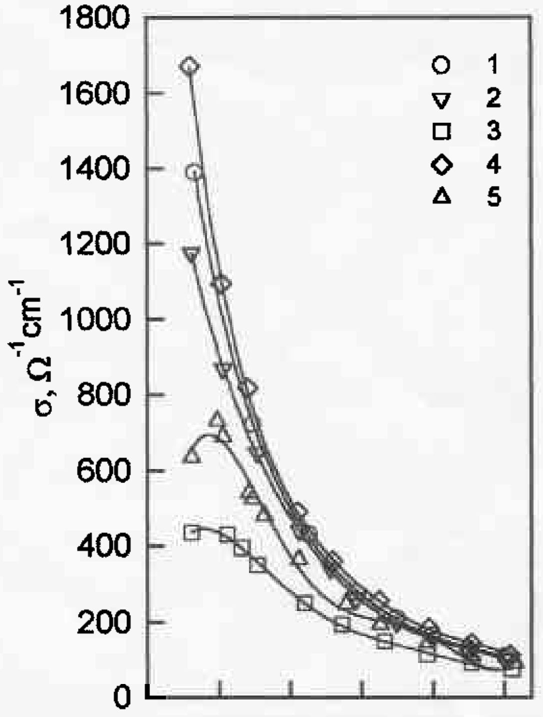

Figure 2. Electrical conductivity of undoped samples of $PbTe_{1-x-y}Se_xS_y$ solid solutions. 1 - x=y=0.025; 2 - x=y=0.05; 3 - x=y=0.1; 4 - x=0.1, y=0; 5 - x=0, y=0.1.

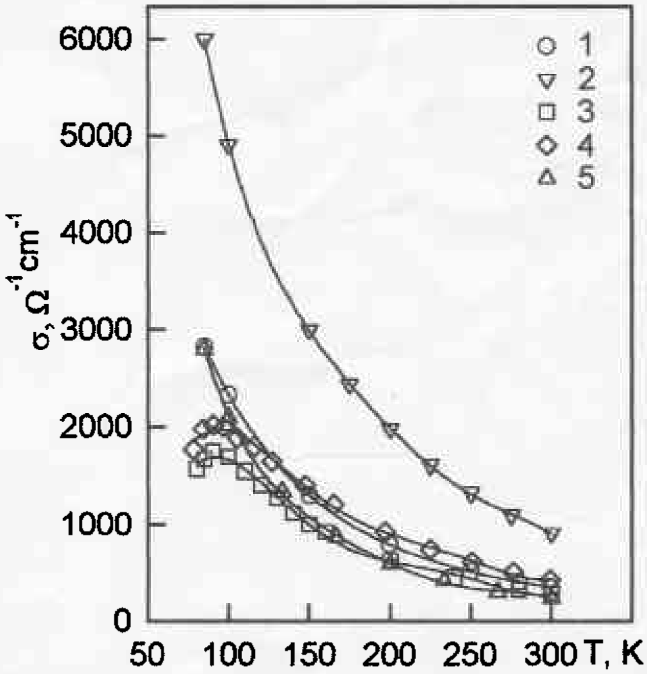

Figure 3. Electrical conductivity of doped samples of $PbTe_{1-x-y}Se_xS_y$ solid solutions. 1,2 - x=y=0.05; 3,4 - x=y=0.1; 5 - x=0.1, y=0; $n(10^{18}cm^{-3})$ = 1,3 – 2; 2 – 5; 4 – 3.3; 5 – 1.4.

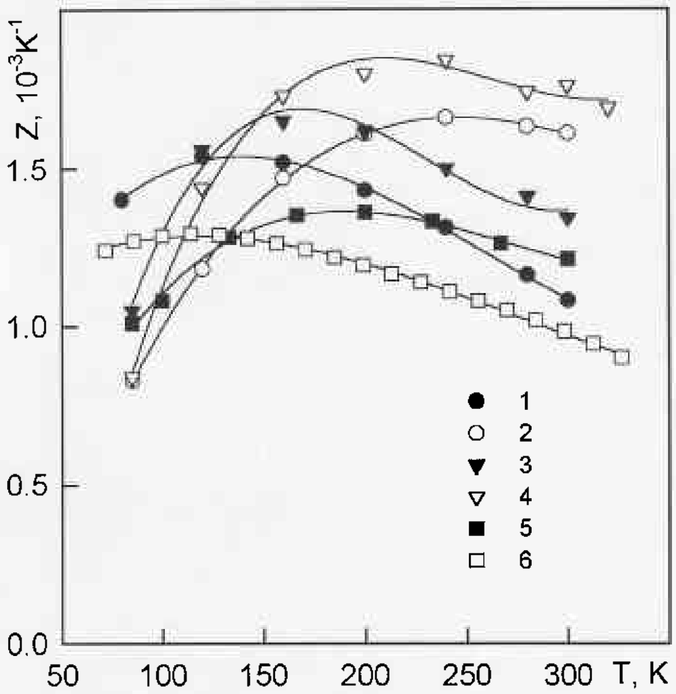

Figure 4 Thermoelectric figure of merit of the samples of PbTe$_{1-x-y}$Se$_x$S$_y$ solid solutions: . 1,2 - x=y=0.05; 3,4 - x=y=0.1; 5,6 - x=0.1, y=0; n(10^{18}cm^{-3}) = 1, 6 – 0.5; 2, 3 – 2; 4 – 3; 5 – 1.4.

Thus, the off-center positions of S atoms are favorable factor for the increase of figure of merit, but similar to the filling voids in crystal structure they influence strongly not only to the phonon subsystem but on the electron subsystem either.

Mobility edge conception

The thermoelectric properties of a material with mobility edge were for the first time described in the papers [3, 4]. A simply model was used: in usual parabolic band all current carriers with the energy less than some critical energy E_c have no mobility (u=0). At the energy higher than E_c, all properties are described by the usual band laws with the current carriers scattering by acoustic phonons. It was shown that due to optimization of the Fermi level relatively to the mobility edge E_c it is possible to increase power parameter $S^2\sigma$ four times in comparison with that of the band without the mobility edge. Moreover the Lorents number for the system decreases about twice. So, the creation of mobility edge is a direction for modifying electronic system. The only question arises: "How to do it?" Little bit earlier than the papers mentioned above a paper devoted to increasing the figure of merit in a barrier structure [7] has been published. It was shown that if a flux of current carriers goes across the system of energy barriers it is possible to increase the figure of merit if the distance between the barriers and their height meet the certain conditions. This proposal reminds the modern conception of quantum well structure. The difference between quantum well structure and an energy barrier structure is in 1) the direction of current carriers flux and 2) the height of energy barriers. In quantum well structure the current carriers flux is directed along the barriers of infinite height. One could suggest to make such a barrier structures by consecutive sputtering of different materials. May be such variant of energy band structure was realized in the material of ZT = 2.4 prepared by R.Venkatasubramaniam with coworkers [8]. The disadvantage of consecutive sputtered material is that it is thermodynamically unstable and at some temperature diffusion has to destroy it. A natural conductive layered structure could be a base for creation an effective thermoelectric. The necessary condition is: a method allowing to change the positions and thickness of the layers has to exist.

Higher silicides of transition metals.

There is a group of materials having good enough thermoelectric properties. It contains ruthenium sesquisilicide, chromium and iron disilicides and higher manganese silicide. All these materials have many common features. They have similar structures and not usual conduction mechanism. The anisotropy of transport properties is found in all of them except, may be, iron disilicide. They have solid state phase transitions except, may be, chromium disilicide [9]. The most studied material of this group is higher manganese silicide (HMS), may be because it has the highest figure of merit among these materials [10].

There are few crystal structures of HMS: Mn_4Si_7; $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$ etc. The region of existence of HMS is $MnSi_{1.71-1.75}$. These crystal structures can be obtained due to little change of the ratio N_{Si}/N_{Mn}. A peculiarity of HMS is that all crystals prepared by directed crystallization have a regular system of the second phase (MnSi) precipitations. These precipitations does not change the orientation of the blocks of the main phase. So, in the experiments on neutron diffraction such a crystal is seen as a single crystal. The HMS crystal can be described as a regular system of blocks, oriented in the same direction, and separated by so-called soliton walls. Some of soliton walls are the seeds for the second phase precipitating. Thermoelectric properties of HMS are determined by the mentioned above regular system of blocks and soliton walls [11]. Thermoelectric figure of merit for HMS is higher in the direction of its tetragonal axis, that is in the direction ortogonal to the planes of soliton walls. So, HMS could be considered as a natural barrier structure. Is it possible to change the properties of this structure or not?

Reconstruction of HMS barrier structure

We have studied the influence of Ge on HMS properties. Earlier it was shown that Ge influence strongly on the precipitation system of HMS [12] and its thermoelectric properties [13]. The interconnections among microstructure and thermoelectric properties was studied for the first time in [14].

Above-mentioned papers showed, that Ge doping results in increasing amount of stripes per unit length of crystal. Some samples have cross-linked structure of stripes [12, 15]. Now one can say that high speed of crystallization can result in such a structure.

In the work [14] the influence of replacement of silicon (up to 1 atomic percent) by Ge on the microstructure and kinetic properties of HMS single crystals was investigated. Samples for measurements were prepared by Bridgeman technique. Crystallization rate was 4mm/h.

Microstructure of the samples can be seen in optical microscope in polarized light. On the majority of samples the system of stripes was observed to be close to regular, and orientation of stripes was constant along all length of a sample accessible to observation (about 2 cm.). On the samples with the high germanium contents (~1 atomic percent) block structure was observed. The length of the greatest block even in this case exceeded 1 cm. Similarly to the researches carried out earlier, in our samples the increase of germanium contents also results in reduction of the distance between strips (fig. 5,6).

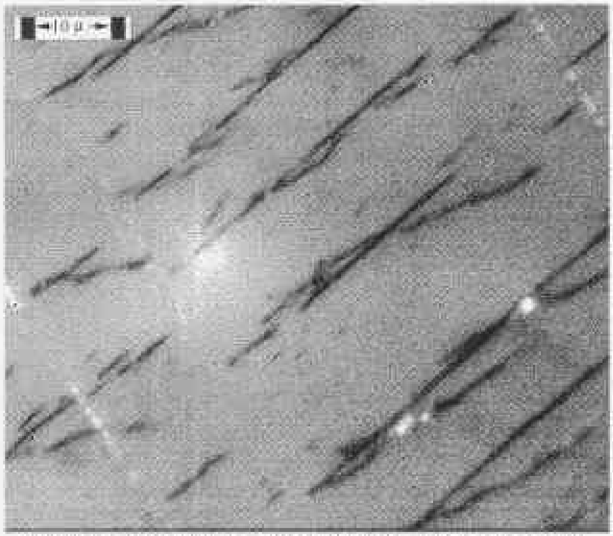

Figure 5. Microstructure of $Mn(Si_{0.995}Ge_{0.005})_{1.75}$ [14]

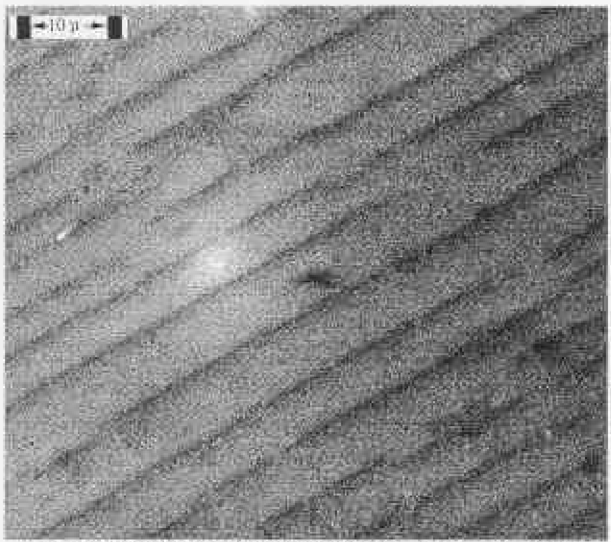

Figure 6. Microstructure of $Mn(Si_{0.99}Ge_{0.01})_{1.75}$ [14]

We investigated the temperature dependencies of Seebeck coefficient and electrical conductivity in the temperature interval 80-1000K and thermal conductivity in the temperature interval 300-1000K. At room temperature Ge doping practically does not change Seebeck coefficient, but rise electrical conductivity in the direction perpendicular to C axis.

On Fig.7, 8 the temperature dependencies of relational electrical and thermal conductivity of $Mn(Si_{1-x}Ge_x)_{1.75}$ along and across C axis are shown.

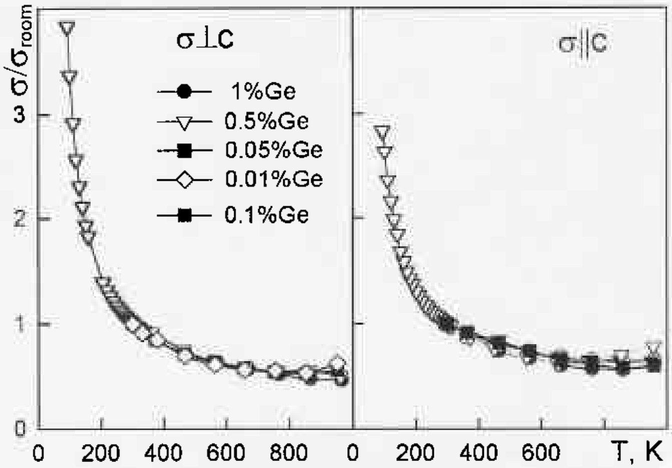

Fig. 7. Temperature dependencies of electrical conductivity of $Mn(Si_{1-x}Ge_x)_{1.75}$ along and across C axis. [14]

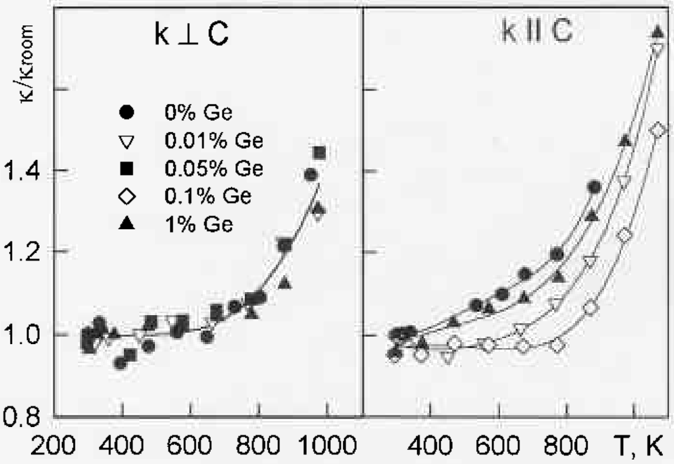

Fig. 8. Temperature dependencies of thermal conductivity of $Mn(Si_{1-x}Ge_x)_{1.75}$ along and across C axis. [14]

The examination of this and earlier papers shows, that Seebeck coefficient in the direction perpendicular to C axis doesn't depend on Ge doping, but electrical conductivity grows up when the concentration of Ge increasing. As Fig.7 shows, Ge doesn't change the type of temperature dependence of electrical conductivity. The same we can say about HMS thermal conductivity in the direction perpendicular to C axis (Fig.4). In the direction parallel to C axis a small quantity of Ge makes thermal conductivity constant up to 700-800K contrary to that of pure HMS. This change of thermal conductivity temperature dependence allows to increase essentially thermoelectric figure of merit of Ge-doped HMS.

Other silicides

One can say that natural barrier structure exists only in HMS. It is wrong. In [16] it was shown that the system of regular precipitation can exist in high temperature modification of iron disilicide crystals. The precipitations became more regular when pulling rate decrease. Contrary to HMS these precipitations are similar to pipes oriented along crystallisation axis (at least at not very low pulling rate).

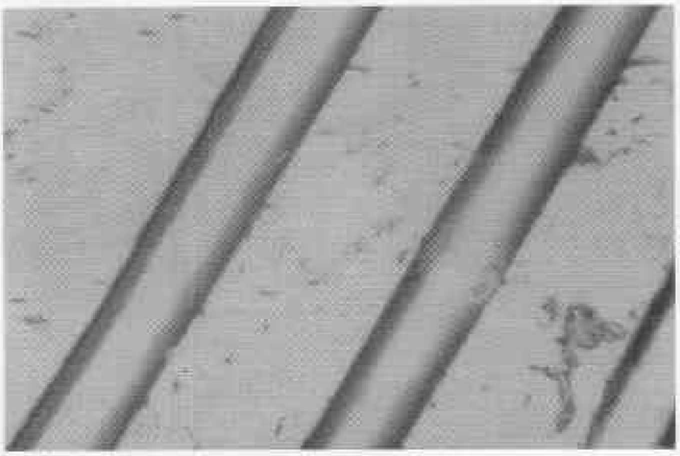

Figure 9. FeSi precipitations in α-$FeSi_2$ (The plane along the crystallization axis) [16]

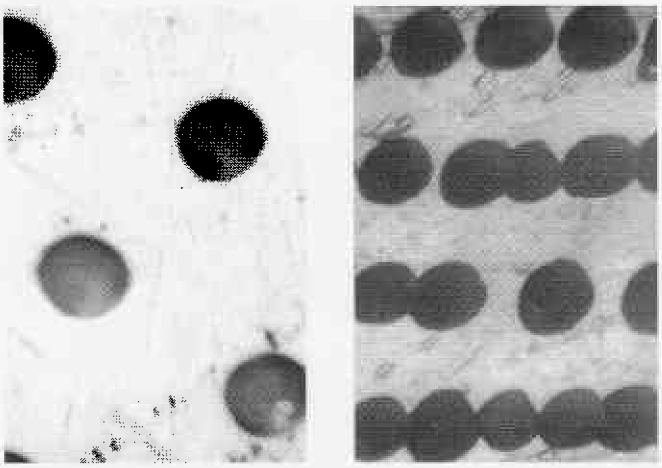

Figure 10. FeSi precipitations in α-$FeSi_2$ (The plane across the crystallization axis) [16] left figure – high crystallization rate, right one – low crystallization rate.

It was checked by X-ray topography and neutron diffraction that the crystal orientation of main phase is practically the same in various parts of the sample as the figure 11 shows. The curve of neutron diffraction of α-$FeSi_2$ sample made at the crystallization rate ~ 4 mm/hour is shown in this figure. Although α-$FeSi_2$ is not a thermoelectric but the results of its study show that natural barrier structure could be found in other higher silicides. Moreover, after converting α-$FeSi_2$ into β-phase there are some remains of α-$FeSi_2$ microstructure (Fig.12). Such thermoelectrics as $CrSi_2$ and Ru_2Si_3 have to be studied in more detailes, to understand the nature of anisotropy of transport properties in these materials. Probably the mentioned anisotropy and especially Seebeck coefficient anisotropy can be connected with the existence of some kind of energy barrier system in these materials.

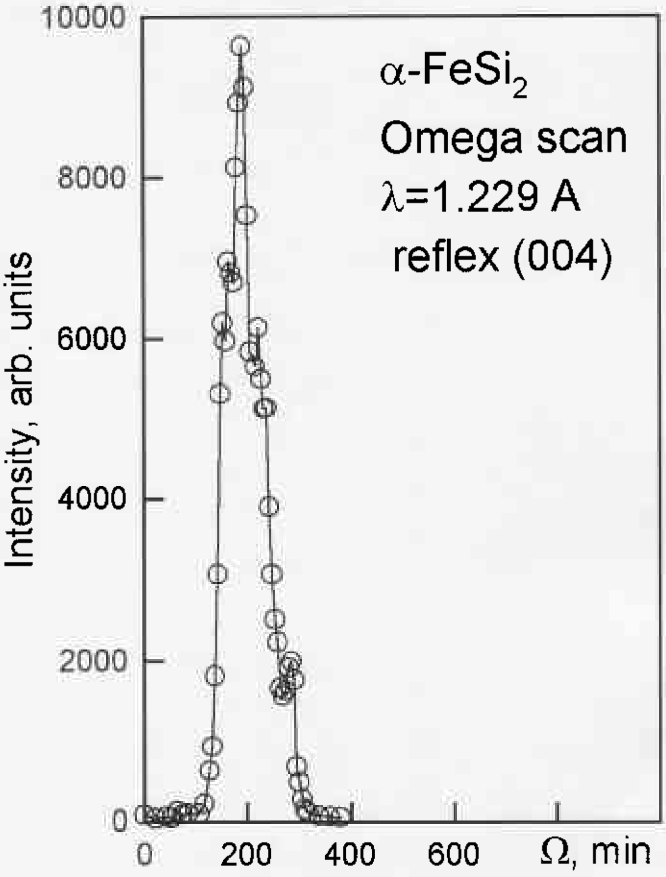

Figure 11. Results of neutron diffraction experiment for α-$FeSi_2$. The sample size are: 12 mm in diameter and 30 mm in length. Crystallization rate ~ 4 mm/hour.

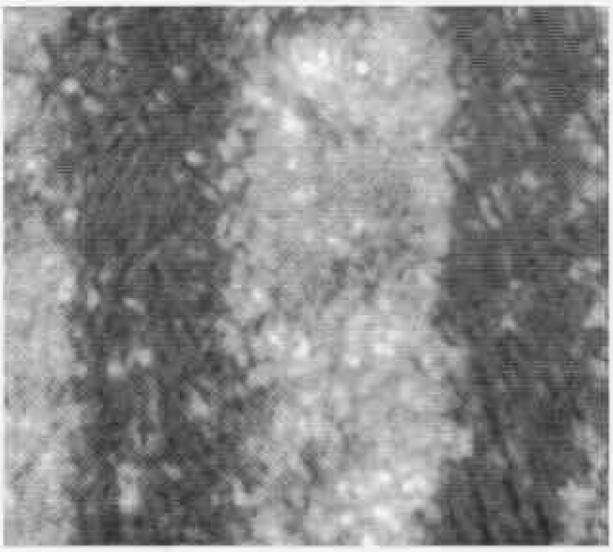

Figure 12. Microstructure of β-$FeSi_2$ sample in polarised light. [16]

Conclusion.

First of all we can conclude that it is impossible to change electron or phonon subsystem without changing the second one. To produce better thermoelectric it is necessary to find optimum action on the both systems. The systems with unstable atom positions can be used for both variants of the increase of figure of merit.

Acknowledgments

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