AZƏRBAYCAN MİLLİ ELMLƏR AKADEMİYASININ XƏBƏRLƏRİ
Fizika-riyaziyyat və texnika elmləri seriyası, 2001 №2,5

УДК 621.315.592

PHONON PROCESSES in GaSe SINGLE CRYSTALS

I.M.ALIYEV

Institute of Physics, National Academy of Sciences of the Azerbaijan
370143, Baku, H.Javid ave., 33

The results are presented of an investigation of the heat conductivity and thermal diffusivity of GaSe layer single crystals doped with up to 0,5at % tin. Measurements were conducted parallel and at right angles to the layers in the temperature range from 100 to 300K. A severe anisotropy of phonon heat conductivity has been revealed. The data obtained are interpreted on the basis of the theory of phonon scattering by point defects.

Gallium selenide (GaSe) crystallizes in layer structure characterized by a strong covalent bond inside the layer and a weak Van-der-Waals bond between the layers. Such a structure affects both the electron and phonon processes. The latter can be studied by investigating the heat conductivity. Such investigations make it possible to obtain important information on the mechanisms of heat transfer, the interphonon processes, the interaction between phonon and point defects, etc.

The thermal properties of GaSe are still not clearly understood. The heat conductivity of GaSe single crystals was elsewhere [1,2,9]. Those studies showed an anisotropy of the heat conductivity coefficient and the part played by acousto-optical interactions in the heat conductivity of GaSe. The effect of various impurities on the heat conductivity of GaSe is not completely understood. Investigations of the heat conductivity of GaSe with different degrees of doping provide interesting information on phonon scattering by phonons and impurities. Heat-transfer data can contribute to the understanding of the part played by impurities in this material.

The present report deals with an investigation of the heat conductivity (χ) and thermal diffusivity (α_0) of gallium selenide, depending on the degree of doping with up to 0,5 at. % tin and on temperature in the range from 100 to 300K.

Introduction of impurities belonging to group IV elements, such as tin brings about a severe growth of the resistance and photosensitivity of GaSe. Tin is a compensating donor impurity in GaSe [3,4].

Thermal diffusivity was measured by a method suggested in an earlier report [5]. This method was used to measure the thermal diffusivity of GaSe at a light incidence perpendicular to the layers. The use of the pulse method was impossible, because it was difficult to provide a contact between the thermocouple and the specimen in the direction parallel to the layers. That is why in this direction the heat conductivity was measured by a stationary method. When using the method of light pulse heating, one should take into account the effect of light on heat conductivity, theoretically discussed elsewhere [6].

In our measurements the photothermal effect was eliminated by applying a thin layer of soot to the front surfaces of the specimens.

On the basis of the experimental values of α_0 the heat conductivity coefficient χ was calculated with the formula

$$\chi = \alpha_0 C \rho \qquad (1)$$

The values of heat capacity **C** and density **ρ** at different temperatures were taken from another report [7].

Because of the low values of electrical conductivity σ of GaSe ($\sigma=10^{-7}$ to $10^{-10}\Omega^{-1}cm^{-1}$) the electronic part of heat conductivity, calculated according to the Wiedemann - Franz law $\chi_{el}=L\sigma T$ (L is the Lorenz number) is negligibly low, and in the temperature region under study the lattice heat conductivity is equal to the total heat conductivity.

Fig.1 gives the temperature dependences of the heat conductivity of GaSe single crystals for the directions along (χ_{prl}) and across (χ_{ppd}) the layers. The curve 5 corresponds χ_{prl}(T) and curve 1 - χ_{ppd}(T) for the undoped sample. 2, 3, 4 curves represent χ_{ppd} (T) for GaSe with the impurities 0,05; 0,1; 0,5at.% of Sn, respectively.

As seen, a severe anisotropy of the heat conductivity coefficient is observed in the undoped gallium selenide: at 300K $\chi_{prl}/\chi_{ppd}\approx 40$ (χ_{prl} and χ_{ppd} are heat conductivities for the directions parallel and perpendicular to the C axis, respectively). This is due to the difference in chemical bonds between the atoms inside the layers and between the layers. The results obtained for GaSe are in good agreement with published data [1].

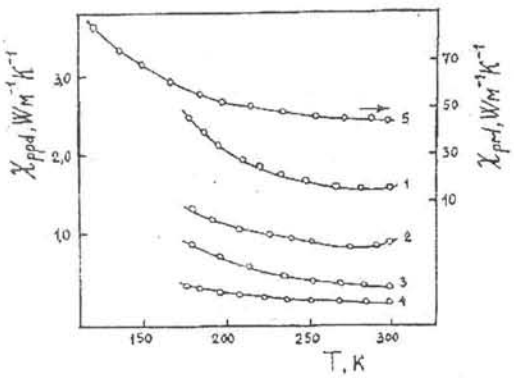

Fig.1.
Temperature dependences of heat-conductivity coefficients along (χ_{prl}) and across (χ_{ppd}) the GaSe layers: 1, 5–GaSe; 2–CaSe:0,05at.% Sn; 3 -CaSe:0,1at.% Sn; 4-CaSe:0,5at.% Sn. 1–4 at right angles to GaSe layers; 5–parallel to layers.

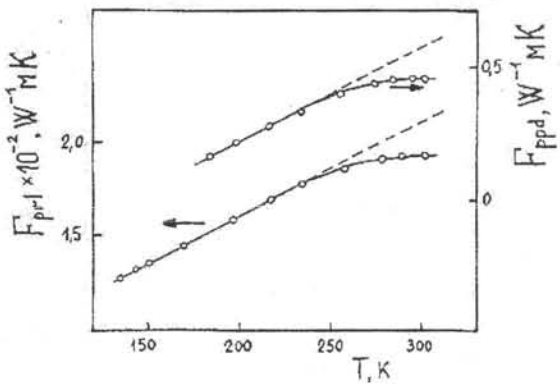

Fig.2.
Temperature dependences of the lattice thermal resistance along (F_{prl}) and across (F_{ppd}) the GaSe layers.

Fig.2 depicts the temperature dependences of the lattice thermal resistance $F=1/\chi$. In undoped gallium selenide specimens the thermal resistance of the lattice varies linearly (F~T) up to a temperature of 230K in both directions, which points to the leading part played by three-phonon umklupp processes. Above 230K a deviation of the F(T) dependence from the linear trend is observed, i.e. an additional heat conductivity $\Delta\chi$ exists. It is known that optical phonons can take part not only in the processes of interaction with acoustic phonons, giving rise to thermal resistance, but also in the heat transfer, if there is a dispersion of the optical branch of the thermal spectrum. The additional heat conductivity $\Delta\chi$ of the GaSe single crystal above 230K is likely to be due to the heat transfer by optical phonons.

The Klemens formula [8,] was used to calculate the lattice heat conductivity for doped specimens with due regard for three-phonon umklupp processes and phonon scattering by point defects

$$\chi_{lattice} = \chi_0 \omega_0/\omega_D - \mathrm{arctg}\,\omega_D/\omega_0 , \qquad (2)$$

where $(\omega_0/\omega_D)^2 = K/2\pi\chi_o \upsilon\, \omega_D A$. Here, χ_o is the heat conductivity in the absence of impurities, ω_D is the Debye frequency, υ is the sound velocity, ω_0 is the frequency at which $\tau_{ph.ph}=\tau_{ph.imp.}$, where $\tau_{ph.ph}$ and $\tau_{ph.imp}$ are relaxation times of phonon-phonon and phonon-impurity processes, respectively, and A is a parameter taking into account the effect of variation of the mass and the elastic properties when one atom is substituted by another one

$$A = \frac{x(1-x)}{4\pi\upsilon^3 N}\left[\left(\frac{\Delta M}{M}\right)^2 + \varphi\left(\frac{\Delta\delta}{\delta}\right)^2\right] \qquad (3)$$

where x is the impurity-concentration fraction, φ is a parameter depending on the elastic properties of the medium, $\Delta M / M$ is the local variation on density ($\Delta M / M = M_{Ga}-M_{Sn}/M$; $M=M_{Ga}-M_{Se}/2$); $\Delta\delta/\delta$ is the local variation of the value of interatomic forces being associated with the substitution of the base atoms by impurity atoms, and N is the number of atoms in a unit volume. Only the local variation of density was taken into account by use while performing the calculations.

Fig.3 shows the results of calculations (curve 1) and experimentation (curve 2) at 250K in the form of the dependence of χ on the degree of doping with tin. The experimental curve runs much lower than the estimated curve. The observed difference points to the fact that a tin impurity in a GaSe single changes severely the elastic properties of the crystals. The experiment was carried out in the direction perpendicular to the layers. Such a severe variation of the lattice heat conductivity is likely to be indicative of the fact that the tin impurity substituting the gallium atoms inside the layer can, nevertheless, affect the interaction between the layers by loosening the lattice.

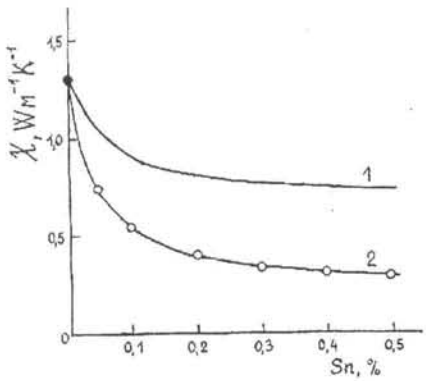

Fig.3.
Heat conductivity dependences of GaSe as a function of doping:
1- calculation data (the Klemens theory); 2- empirical data.

1. G.D.Guseinov, A.I.Rasulov, *Phys.Stat.Sol*, **8** (1966) 11.
2. G.D.Guseinov, A.I.Rasulov, E.M.Kerimova, M.Z.Ismailov, *Phys.Stat.Sol.*, **19** (1967) K7.
3. R.H.Bube, E.L.Lind ,*Phys.Rev.*,**115** (1959) 1159.
4. N.A.Aliyev, B.G.Tagiyev, A.R.Gajivev, *Preprint of the Institute of Physics Academy of Sciences of Azerbaijan, Baku*, **6** (1979).
5. M.I.Aliyev, R.E.Guseinov, D.G.Arasly, *Inzh.Fiz.Zhurn.*, **22** (1972) 1055.
6. W.W.Gartner, *Phys.Rev.*, **122** (1961) 419.
7. K.K.Mamedov,I.G.Kerimov,V.N.Kostryukov,M.I.Mekhtiyev,*Fiz.Techn.Polupr.*,**1** (1967) 441.
8. P.G.Klemens, *Phys.Rev.*, **119** (1960) 507.
9. I.M.Aliyev, *In Proceeding "5th Asian Thermophysical Properties Conference", Seoul,Korea* (1998) 318.

GaSe MONOKRİSTALLARINDA FONON PROSESLƏRİ

İ.M.ƏLİYEV

GaSe monokristallarının istilik və temperatur keçiriciliyi tədqiq edilmişdir. Qalay aşkarları ilə legirə olunmuş kristallarda laylara parallel və perpendikulyar istiqamətlərdə tədqiqatlar aparılmışdır. Fonon istilik keçiriciliyin anizotropluğu göstərilmişdir. Alınmış nəticələr fononların nöqtəvi defektlərdən səpilməsi baxımından izah olunmuşdur.

ФОНОННЫЕ ПРОЦЕССЫ В МОНОКРИСТАЛЛАХ GaSe

И.М.АЛИЕВ

В монокристаллах GaSe исследованы теплопроводность и температуропроводность. Исследования проведены в монокристаллах GaSe, легированных оловом, параллельно и перпендикулярно слоям. Показана анизотропия фононной теплопроводности. Полученные результаты объясняются с точки зрения рассеяния фононов на точечных дефектах.

Редактор: Х.Аждаров