

ELECTRICAL AND THERMAL PROPERTIES OF PbTe DOPED WITH MAGNETIC IMPURITIES*

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ABSTRACT. Thermoelectric power, thermal conductivity and electrical resistivity of *p*-type PbTe doped with iron, manganese, tellurium and *n*-type PbTe doped with gadolinium and manganese are reported. Iron acts as donor or acceptor depending on the impurity concentration. Manganese was found to be a donor dopant. The variation of these parameters with temperature is discussed. The resistance was found to behave in an anomalous manner both in the pure as well as doped *p*-type specimens. The possible causes of the observed behaviour in these systems are discussed.

INTRODUCTION

There has been considerable interest in the thermoelectric properties of PbTe, because of its value in power generation. Present day interest in thermoelectricity is to obtain a high figure of merit by incorporating suitable impurities. The studies have been hitherto confined to non-magnetic impurities. The presence of paramagnetic impurities may, however, drastically alter carrier concentration and influence other physical properties such as thermal conductivity, thermoelectric power and electrical resistivity (Narasimhan *et al*, 1965).

In the present paper we report the thermoelectric properties of *p*- and *n*-type PbTe doped with paramagnetic and neutral impurities. The possible causes of the observed anomalous resistance of *p*-type PbTe are also discussed.

METHOD OF PREPARATION OF SPECIMEN AND MEASUREMENT

Lead (A. E. C. Trombay), tellurium, iron, manganese and gadolinium were all spectroscopically pure (as supplied by Johnson and Mathey). The elements were taken in their proper proportions and heated at a temperature of 1000°C for 24 hours in an evacuated silica tube and quenched at 800°C. The homogeneous regions tested by thermoelectric probing were cut off and pressed to form cylindrical pellets. The pellets so prepared (usually of length 12 mm and diameter 10 mm) were sintered in vacuum at a temperature of 650°C for 24 hours. These sintered blocks were nickel plated at the two ends and used for measurement.

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For preparing the doped samples the required quantity of the dopant was added to PbTe and the compound remelted. The same treatment as mentioned for the undoped compound was given.

The measurements of thermoelectric power, electrical conductivity and thermal conductivity were carried out by means of z meter technique (Harman 1958, Harman *et al* 1959). The details of the apparatus and measurement are discussed elsewhere (Narasimhan 1967).

RESULTS AND DISCUSSION

The results of each system are discussed separately.

PbTe doped with iron

The variations of thermoelectric power, thermal conductivity and resistivity with temperature are shown in table 1.

When p -type PbTe was doped with iron the conductivity changed from p -type to n -type depending on the concentration of the dopant. When 0.1 at. % iron is added to p -type PbTe the thermoelectric power (α) changed its sign relative to that for the pure system. On increasing the concentration of iron to 0.5 at % thermoelectric power increases to a large value while the sample remained n -type.

The change in the sign of thermoelectric power on adding iron may be due to donor action of iron. Iron atoms go into the solution as iron telluride (probably as FeTe_2). These iron telluride molecules substitute for the PbTe molecules thereby vacant sites are created. Atoms from lead excess occupy these vacant sites and as the valence electrons of the lead atoms are not involved in chemical bonding they are easily ionized to the conduction band. This mechanism by which impurity atoms dope is responsible for the n -type conductivity. Increasing the concentration of lead leads to substitution of more and more PbTe molecules and increase of electron concentration. On the other hand large increase of added dopant leads to p -type conductivity. This may be explained in the following way. In a crystal there are always certain number of lead and tellurium ion vacancies. On adding small concentration of iron, the lead vacancies created are filled up by the excess lead atoms, thereby maintaining in equilibrium the concentration of lead vacancies. If the vacancies created by the iron atoms is large compared to the excess lead atoms present then the number of lead vacancies are more than the tellurium vacancies. The tellurium atoms surrounding these lead vacancies have two electrons less which they take up from the environment and thus the holes are created (Kobayashi *et al* 1964). Somewhat similar situation exists in Bi_2Te_3 also (Ainsworth 1956). Excess bismuth atom gives n -type conduction, whereas, limited excess concentration leads to hole conductivity.

Fritts (1960) observed that iron acts like a neutral impurity in PbTe. Brebrick *et al* (1962), on the other hand, found that iron acts like a low lying donor from his measurements on Te saturated PbTe doped with iron. However, the thermoelectric properties of these doped compounds have not been reported.

The thermoelectric power decreases on adding 0.1 at. % iron but increases to a large value at 0.5 at % iron additions. At higher concentrations the number of electrons also increases because originally we have a *p*-type semiconductor and we are adding *n*-type impurity. This results in the compensation of acceptors and when the donor concentration is large we have enough donors to give sufficient electrons to observe a high thermoelectric power. At 2 at. % iron concentrations, as discussed above, iron acts like an acceptor and hence increase in the concentration of holes and large thermopowers.

Thermal conductivity (*K*) decreases on adding iron. This decrease is perhaps due to the scattering of phonons by the added impurities. We can calculate the scattering crosssection for the impurity atom by using Ioffe's formula (Ioffe *et al* 1960). According to this

$$\frac{K_{L(0)}}{K_L} = 1 + \frac{N}{N_0} \cdot \theta \cdot \frac{l_{T(0)}}{a}$$

where *N* is the addition concentration, *N*₀ is the total atomic concentration, *a* is the distance between two neighbouring atoms in the lattice, *l*_{*T*(0)} is the mean free path of the phonon in the undoped specimen, *θ* is the factor in the expression *S* = *θa*² where *S* is the scattering cross section. *K*_{*L*} and *K*_{*L*(0)} are the lattice thermal conductivity with and without addition of second component. *l*_{*T*(0)} can be calculated by using the kinetic formula

$$K_L = \frac{1}{3} C_V \bar{V} l_{T(0)}$$

where *C_V* is the specific heat per unit volume and *V̄* is group velocity of phonon. The value of *C_V*, *a* and *V̄* were taken from the table of Ioffe *et al* (1960). *K_L* was calculated by subtracting the electronic component of thermal conductivity from the measured thermal conductivity by utilizing the Weidemann-Franz ratio. The values of *θ* so calculated are shown in table 2. The value of the scattering cross section is higher at 273.1°K than at room temperature.

The resistivity of all the *p*-type samples and one of the *n*-type sample viz., PbTe doped with 0.1 at. % iron showed increase of resistivity with decrease of temperature. Putley (1955) observed this type of behaviour in his *p*-type samples and suggested that these may be due to the presence of impurity levels situated at 0.1 eV above the valence band. He observed this behaviour in five of the *p*-type samples and in one of his *n*-type samples S21C also. In *n*-type PbTe the impurity level is considered to be situated at 0.1 eV from the conduction band.

Shogenji *et al* (1957) reported that a sample of p -type PbTe heat treated with copper showed the anomalous resistivity behaviour. Kanai *et al* (1957) have also reported that a sample of p -type PbTe exhibited this anomalous behaviour. In all these cases the Seebeck coefficient was not reported. In the present measurements the type of conductivity was judged only by the Seebeck coefficient measurement. There was no change of sign observed throughout the temperature range investigated. It is most likely that Hall coefficient will also behave in a similar way.

The possibility of spurious voltage was tested. The solder was scrapped off and the sample resoldered and the measurements repeated. No changes in the original behaviour were observed. After cooling to liquid air temperature the sample was brought to room temperature. The resistivity was showing the initial value. Hence these observed anomalies are not due to any spurious voltages.

Scanlon (1959) found that a sample of PbS coated with sulphur vapour showed Hall coefficient reversal similar to those of Putley (1955) and Shogenji *et al* (1957). This second sign reversal was observed in the extrinsic region. Scanlon (1959) attributed these to p - n junction, in which an n -type sample is covered on all the surface with a p -type layer. In the present measurements, however, no heat treatment was given to form p - n junction. It is interesting to note that only in p -type PbTe such a behaviour was observed. When p -type PbTe was doped sufficiently with a donor to make it n -type, the anomaly was lost and the resistivity decreased with decrease of temperature. Also, n -type lead telluride prepared by taking 0.2 at. % excess lead did not show the resistance anomaly. Moreover, the treatment given to p -type PbTe and n -type PbTe was identical and it seems unlikely that the anomaly observed in p -type PbTe is due to the presence of p - n layers. A conclusive test was carried out to find out the presence of p - n layers. The samples exhibiting the anomaly were scraped on both the lateral sides to remove some layers. The thermoelectric probe was moved throughout the surface to find out p - n layers. The experiment was repeated for each mm layer removed on both the end as well as lateral sides. There was no change of sign of the cold end terminal. The hot probe has to be connected to the $-ve$ terminal and the cold end to the $+ve$ terminal for current to flow. This proved conclusively that there are no p - n layers.

This suggests that there are impurity levels situated in the forbidden gap and the scattering of carriers by the impurity atoms is important. The appearance of anomaly in p -type PbTe shows that impurity levels are near the valence band and form acceptor levels. From the slopes of log resistivity against temperature the energy levels of the impurity atom is calculated. We assume that the increase of resistivity with decrease of temperature is due to the electrons falling back into the valence band thereby reducing the concentration of holes. The impurity levels in general are situated at 0.1 eV. The value of energy gap E_g was found to

be 0.1 eV as derived on the assumption that there is no compensation and the concentration of donor atoms is very small. The reason as to why *n*-type PbTe do not exhibit the resistance anomaly is that the acceptor levels are all compensated by the donors and with decrease of temperature the resistance decreases because of the interaction of carriers with phonons becoming small.

p-type PbTe-Te

The variations of thermoelectric properties as a function of excess tellurium were studied with a view to finding an optimum composition which gives high figure of merit. The doping was carried upto 5 at. % excess tellurium. Thermoelectric power remains nearly the same with increasing concentration of tellurium. Excess tellurium atoms occupy the tellurium vacancies and accept the electrons from the neighbouring atoms and thus induce *p*-type conductivity. Fairly high concentration of excess tellurium may be introduced into PbTe depending on the heat treatment. The solubility of excess Pb or Te in PbTe is not more than one hundredth of one percent in pure samples. By quenching at elevated temperatures it should, however, be possible to introduce large excess. Since all the samples in the present measurements are quenched at 800°C it is likely that large excess could be incorporated. Fritts (1960) observed that any precipitation of excess phase will lead to increase in resistivity at room temperature. For the highly doped sample i.e. 5 at. % excess tellurium an increase in the resistivity was observed at room temperature (fig. 1). It is likely that in this sample some tellurium has precipitated out and these rejected tellurium atoms have collected at dislocations during freezing.

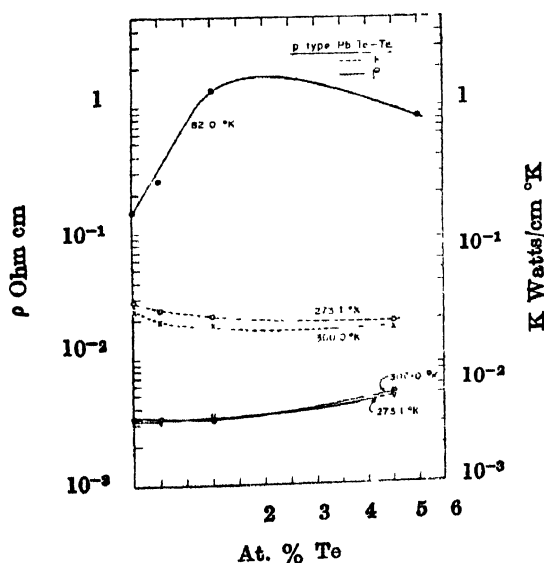


Fig. 1. Variation of electrical resistivity (ρ) and thermal conductivity (K) for various concentrations of tellurium doped on *p*-type PbTe.

Thermal conductivity decreases (fig. 1) with increasing concentration of excess tellurium due to the scattering of phonons by tellurium impurities. The value of scattering cross section is shown in table 2. The figure of merit is highest for the sample doped with 0.5 at. % Te showing thereby that at this concentration we have effected a decrease in thermal conductivity without affecting the resistivity.

p-type PbTe-Mn

Manganese is a donor dopant in PbTe. Owing to this, thermoelectric power changes sign and becomes negative.

The low values of thermoelectric power (table 3) suggest the onset of degeneracy and the resistivity increase observed is due to impurity scattering of carriers. In view of the high concentration of manganese added X-ray powder pattern was analysed to find out the presence of second phase. The specimen was found to be quite homogeneous and no extra lines from the impurity atom could be found.

n-type PbTe-Gd

n-type PbTe was prepared by taking 0.1 at % excess lead over the stoichiometric composition. To this various amounts of gadolinium were added. The results of the measurement are shown in the figures. Figs. 2, 3 and 4 show the variation of thermoelectric power, thermal conductivity and electrical resistivity as a function of impurity additions at various temperatures.

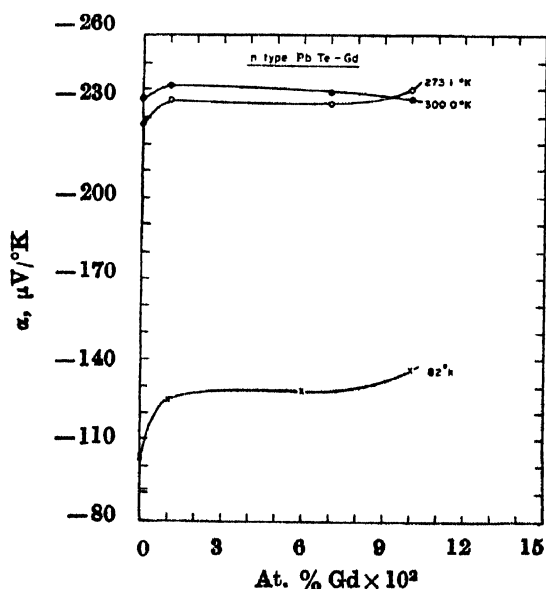


Fig. 2. Variation of thermoelectric power of *n*-type PbTe doped with various concentrations of Gd at different temperatures.

In the undoped specimen thermoelectric power decreases with decrease of temperature as is expected from the theory. The increase in the value of thermoelectric power at low temperatures with increasing gadolinium concentration may

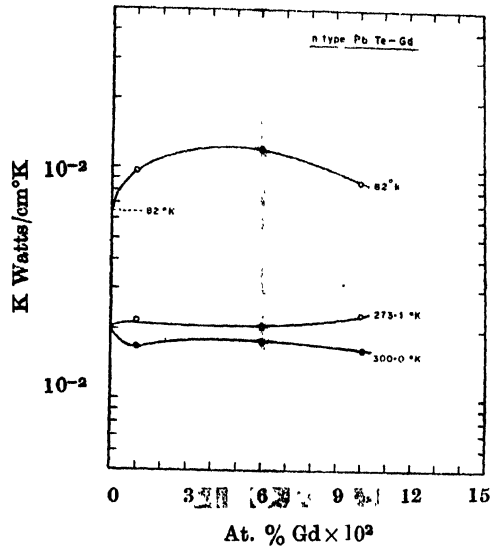


Fig. 3. Variation of thermal conductivity of *n*-type PbTe doped with various concentrations of added Gd at different temperatures.

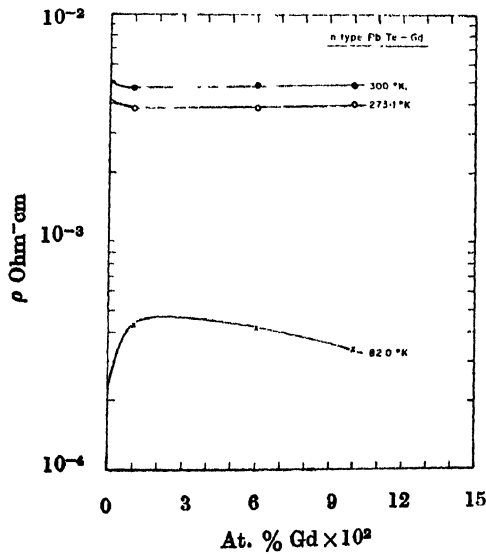


Fig. 4. Variation of resistivity of *n*-type PbTe doped with various concentrations of gadolinium at different temperatures.

be due to the increase in the value of r in the expression for thermoelectric power (α)

$$\alpha = \pm \frac{k_B}{e} \left(A + \ln \frac{2(2\pi m k_B T)^{3/2}}{h^3 n} \right) \quad \dots (1)$$

where k_B is Boltzmann constant, $A = r + 2$; r depends on electron scattering mechanism. With increasing concentration of gadolinium, the scattering of electrons increases. Alternatively, gadolinium acts like a trapping centre for holes leading to the increase in the thermoelectric power of electrons.

The undoped specimen has a $T^{-2.5}$ dependence on mobility. If we consider the acoustic mode lattice scattering then the mobility should have a $T^{-3/2}$ dependence. Perhaps this deviation could be explained if we considered a mixture of acoustic and optic mode scattering and interband transition of charge carriers, effected by these. Based on these assumptions Krishnamurthy *et al.* (1965) arrived at an expression

$$\mu = \mu_{(0)}^{(0)} T^{-5/2} \quad \dots (2)$$

where $\mu_{(0)}^{(0)}$ is the temperature independent factor. In this formulation two phonon processes involving one acoustic and one optical phonon and two optical phonons were considered. The agreement with the experimental result suggests that interband transition and both acoustic and optic mode scattering effects are important for the scattering mechanism in PbTe and other compound semiconductors.

For the doped samples, the mobility has a $T^{-1.9}$ and $T^{-2.0}$ dependence which may be due to the onset of impurity effects. In another paper Krishnamurthy *et al.*, (1966) have given a general expression incorporating two-phonon processes and one phonon impurity induced processes. The total mobility has the form

$$\mu_t = \frac{\mu_0^{(s)} \mu_0^{(0)} T^{-5/2}}{\mu_0^{(0)} T^{-1} + \mu_0^{(s)}} \quad \dots (3)$$

Thus for $\mu_0^{(0)} T^{-1} \gg \mu_0^{(s)}$, the mobility $\mu_t = \mu_0^{(0)} T^{-3/2}$ and for reverse condition $\mu_t = \mu_0^{(s)} T^{-5/2}$. It is clear that in the intermediate regions the exponents on temperature will have values ranging from -1.5 to -2.5 depending on the relative magnitudes of the terms in the denominator.

Thermal conductivity shows an increase with increasing gadolinium additions at 82°K (fig. 3). For the same reason the temperature variation of thermal conductivity in the case of doped samples have much stronger temperature

Table 1
Variation of thermal conductivity, thermoelectric power and electrical resistivity of p-type PbTe doped with iron

Sample No.	Composition	Thermal conductivity			Resistivity ohm cm			Thermoelectric power $\mu\text{V}/^\circ\text{K}$		
		300°K	273.1°K	82°K	300°K	273.1°K	82°K	300°K	273.1°K	82°K
17	Undoped PbTe	2.35×10^{-2}	2.89×10^{-2}	—	(see Table III)			171	185	53
54	0.1 at. % iron	—	—	—	9.64×10^{-2}	1.25×10^{-1}	9.92×10^{-1}	—53	—65	—63
53	0.5 at. % iron	1.71×10^{-2}	1.86×10^{-2}	7.05×10^{-2}	1.04×10^{-2}	8.5×10^{-2}	1.3×10^{-3}	—308	—311	—145
52	1 at. % iron	2.09×10^{-2}	3.17×10^{-2}	—	3.3×10^{-2}	2.3×10^1	1.39×10^{-3}	205	192	86
44	2 at % iron	1.84×10^{-2}	1.96×10^{-2}	—	4.11×10^{-2}	5.19×10^{-2}	4.29	296	326	121

dependence. The undoped specimen has a T^{-1} dependence in agreement with theory (Peierls 1929).

n-type PbTe-Mn

The variations of thermoelectric power and electrical resistivity are shown in figs. 5 and 6. The resistivity increases with impurity concentration with their atoms causing electron scattering leading to a decrease in mobility. But beyond

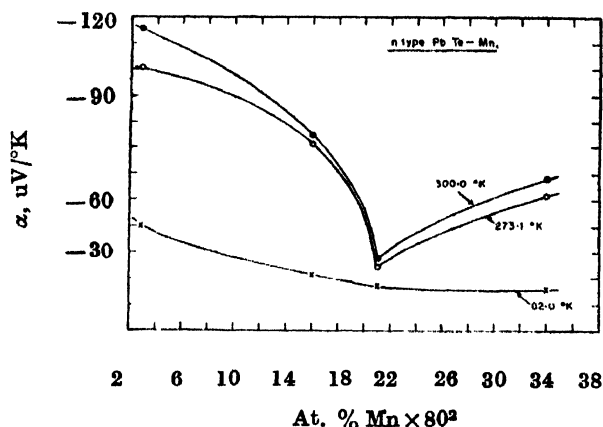


Fig. 5. Variation of thermoelectric power of *n*-type PbTe doped with various concentrations of Mn at different temperatures.

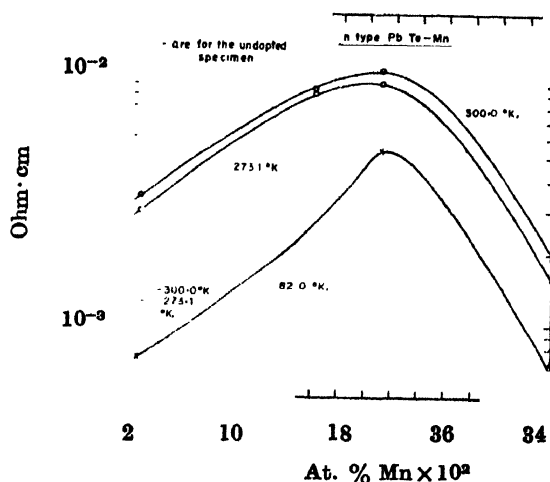


Fig. 6. Variation of electrical resistivity of *n*-type PbTe doped with various concentrations of Mn at different temperatures.

(at 82°K pure *n*-type PbTe has a ρ value 1.34×10^{-4} ohm cm.)

a particular concentration the donor electrons from the impurity atoms lead to increase in electronic conductivity. Thermoelectric power variation with temperature in the case of highly doped sample shows the onset of degeneracy.

The slope of temperature dependence of conductivity decreases in magnitude as the concentration is increased. The experimental curves in most of the cases have T^{-1} dependence. This is perhaps due to the combined effect of impurity and phonon (optical and acoustical) scattering effects.

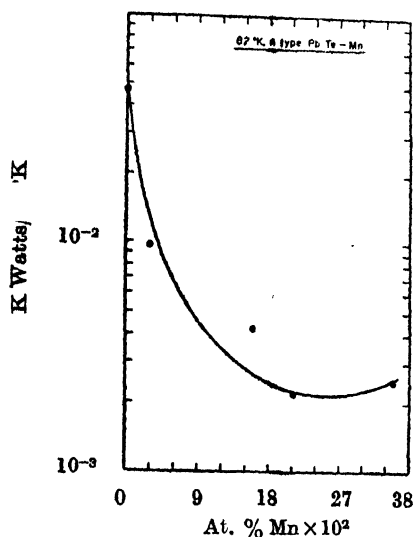


Fig. 7. Variation of thermal conductivity of *p*-type PbTe for various concentrations of Mn at 82°K.

Table 2

Values of the parameter θ and energy gap for various doped samples of *p*-type PbTe.

Sample No.	θ	300°K (θ)	273.1°K (θ)	Energy gap from a plot of $\ln \rho^*$ vs $1/T$
Undoped PbTe	—	—	—	0.08 eV
53 0.5 at. % iron	9.2	11.0	—	—
52 1 at. % iron	1.9	—	—	0.09 eV
44 2 at. % iron	1.4	2.1	—	0.09 eV
16 10 at. % manganese	6.6	23.8	—	—
48 0.5 at. % excess Te	6.0	4.6	—	0.01 eV
50 1.5 at. % excess Te	2.8	3.2	—	0.13 eV
51 5 at. % excess Te	0.9	1.1	—	0.13 eV

* ρ is the electrical resistivity.

Large reduction in the value of thermal conductivity (fig. 7) at 82°K suggests large scattering cross section for the impurity atom. This may be due

Table 3
Resistivity and thermoelectric power of p-type PbTe doped with tellurium and manganese

Sample No.	Composition	Resistivity ohm cm.			Thermoelectric power $\mu\text{V}/^\circ\text{K}$		
		300°K	273.1°K	82°K	300°K	273.1°K	82°K
17	PbTe (undoped)	3.3×10^{-3}	3.3×10^{-3}	1.49×10^{-1}	171	185	53
48	0.5 at. % excess tellurium	3.3×10^{-3}	3.2×10^{-3}	2.58×10^{-1}	189	189	86
50	1.5 at. % excess tellurium	3.3×10^{-3}	3.4×10^{-3}	1.324	175	164	62
51	5 at. % excess tellurium	5.1×10^{-3}	4.9×10^{-3}	8.23×10^{-1}	197	184	61
16	10 at. % manganese	1.26×10^{-1}	1.19×10^{-1}	4.59×10^{-2}	-2	-3	-5

to the substitution of impurity from different group of the periodic table. Klemens (1957) has observed that substitution of divalent magnesium in potassium chloride leads to scattering cross section 100 times more than substitution of monovalent bromine. Paramagnetic susceptibility measurements confirmed that PbTe doped with the Mn, Fe and Gd were paramagnetic.

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