

Optical and magnetic properties of PbTe(Co)

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Far - infrared and magnetic properties of Co doped PbTe ($Z_{Co} = 4 \times 10^{19}$ at./cm³) single crystal are investigated in a broad range of temperature and magnetic fields. Far – infrared reflection spectra were analyzed using a fitting procedure based on the modified plasmon – ionised impurity – phonon interaction model. Together with the strong coupling we obtained three local modes of Co at about 125, 190 and 275 cm⁻¹, which corresponded to the impurity atoms in different valence states. A magnetic measurement shows that doping PbTe by Co causes appearance of paramagnetic properties

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1. Introduction

The lead telluride belongs to the A^{IV}B^{VI} IR – sensitive narrow – gap semiconductor group, which acquire new properties as a consequence of doping [1 – 3]. Depending on the composition, their band gap can vary from almost zero to 0.3 eV [4 – 8], with high value of the static dielectric constant and large difference between ϵ_0 and ϵ_∞ [6].

The doping of A^{IV}B^{VI} semiconductor compounds with transition metal impurities has significant scientific and practical interest due to the possibilities to prepare new materials. PbTe doped with transition elements is perspective material for applications in spintronics. Electrical properties in such manner obtained materials strongly depend on the type and concentration of the added impurity. For instance, Mn in PbTe is electroneutral impurity, and enters PbTe lattice as Mn²⁺. On the other hand, when PbTe is doped with chromium, free carrier concentration n increases to 1.3×10^{19} cm⁻³, and after that slowly decreases to 1.2×10^{19} cm⁻³ with the further increase of the Cr concentration, up to the chromium solubility limit [6]. This means that Cr in small concentration enter the PbTe lattice as donor impurity in the 3+ states. Further, when concentration increases, we have both 3+ and 2+ (as neutral) states, and finally in highly doped semiconductor we have impurities in all three – valence states: 3+, 2+ and 1+ (as acceptor). The mentioned behaviour of transition elements causes strong correlation between an impurity center and the lattice. A change of the electronic state of the impurity center provokes a change of the frequency of the local mode [9].

The coupling of elementary excitations in solids has been investigated by many authors [10 – 12]. Free – carrier absorption by phonon – ionised impurity – plasmon

processes were also studied [9, 13]. These processes are important for polar semiconductors with high static (lattice) dielectric constant and high carrier concentration. Free – carrier absorption consists then in individual – carrier excitations (individual – carrier scattering), as well as in collective carrier excitations (plasmon generation).

Photon – plasmon processes were studied, as a rule, in more general framework of photon – plasma – imperfection (deformation) interactions, in which also individual – carrier excitations were taken into account [14 – 17]. Both nondegenerate and degenerate plasmas were considered. Usually, a theory is formulated starting from the knowledge of dielectric function for free carriers in perfect crystals. Phenomenological approach to this problem is formulated by several authors [17 – 19]. Our approach [18, 19] is based on creating specific dielectric function, which has to explain registered process, while comparisons with parameters obtained by classical approach [10, 11] yield the physical explanation of the processes that are taking place in the doped semiconductors.

Optical properties of the Co doped PbTe are still not sufficiently studied. In this paper, we present the results obtained by using far – infrared spectroscopy (FIR) and magnetic measurements to study properties of the PbTe(Co) with Co concentration of 4×10^{19} at./cm³ single crystal sample. The analysis of the reflection spectra, carried out in wide spectral range, shows that in this system exists the plasmon – ionised impurity – phonon coupling. Together with the strong coupling we obtained three local modes of Co, which correspond to the impurity atoms in different valence states. Magnetic measurements analyses indicated that PbTe alloys doped with Co revealing paramagnetic interaction between magnetic ions.

2. Sample and experiment

Single crystal of PbTe(Co) was grown by the Bridgman method in evacuated sealed 12 – 15 mm quartz tubes with a cone shaped lower end by moving in temperature gradient of 15 – 20 K/cm with a rate of 0.5 – 1 cm/day. The impurity content in the starting mixture was $3.1 \cdot 10^{20}$ at/cm³. The Co concentration in the crystal used here was $4 \cdot 10^{19}$ at./cm³, determined by the chemical analysis. Solubility limit and segregation effect for Co doped PbTe were discussed in more details in Ref. [20].

The structural characteristic was obtained by the XRD powder technique. Sample was examined using a Philips PW 1729 X – ray generator, Philips 1710 diffractometer and original APD software. The radiation source was an X – ray LLF tube with cobalt radiation and graphite monochromator. The radiations were $\lambda_{\text{CuK}\alpha 1} = 0.154178$ and 0.154438 nm. The anode tube load was 40 kV and 30 mA. The slits of 1.0 and 0.1 mm were fixed. For product identification, the MPDS program and JCPDS (ASTM) (Joint Committed on Powder Diffraction Standards) card files were used. The unit cell was calculated by the last square methods. All registered reflections corresponded to PbTe crystals and gave the parameter of cubic unit cell of $a = 0.6455(3)$ nm, which were in good agreement with values cited in literature [21].

The Hall effect and conductivity measurements showed that the crystals exhibited n – type conductivity with the room temperature electron concentration of $6 \cdot 10^{17}$ cm⁻³.

The far – infrared measurements were carried out with a BOMEM DA – 8 FIR spectrometer. A DTGS pyroelectric detector was used to cover the wave number range from 40 to 450 cm⁻¹.

The magnetic measurements were performed using Lake Shore 7229 AC Susceptometer/DC magnetometer.

3. Reflectivity analysis and fitting procedure

The theoretical model of the bulk dielectric function has been discussed by several authors [19, 22]. For a description of the PbTe optical properties simple model for dielectric function were used [23]:

$$\varepsilon = 1 + \chi_{\text{valenceelectrons}} + \chi_{\text{polarphonon}} + \chi_{\text{freecarriers}} \quad (1)$$

The interaction of electromagnetic radiation with plasmons in nonperfect lattices may become comparable or even higher than single – particle scattering [9]. This is especially true for semiconductors with high – static dielectric constant. As a result, the FIR spectra might be interpreted using a frequency dependent dielectric function with no less than two classical oscillators ($l \geq 2$) corresponding to the TO modes superimposed by a Drude

part taking into account the free carrier contribution [11, 12]:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{k=1}^l \frac{\varepsilon_{\infty}(\omega_{LOk}^2 - \omega_{TOk}^2)}{\omega_{TOk}^2 - \omega^2 - i\gamma_{TOk}\omega} - \frac{\varepsilon_{\infty}\omega_p^2}{\omega(\omega + i\gamma_p)} \quad (2)$$

where ε_{∞} is the bound charge contribution and it is considered as a constant, ω_{LOk} and ω_{TOk} are the longitudinal and transverse optical – phonon frequencies, ω_p is the plasma frequency, and γ_{TOk} and γ_p are the phonon and plasma damping.

In the doped PbTe – based systems the pure LO – modes ($\omega_{LO, \text{PbTe}}$) of the lattice are strongly influenced by the plasmon mode (ω_p) of free carriers. As a result a combined plasmon – LO phonon modes (ω_{lj} , $j = 1, 2$) were observed [10], whereupon in the experimental spectra only coupled mode positions were observable. Therefore, the determination of LO mode is connected with the elimination of free carrier influence [17, 18, 24]. Impurity local modes have the same behaviour. This means that impurity local mode, characterized by its characteristic frequency ω_l , can interact with free carriers [25]. In this case there is no separation on TO and LO mode, and as a result, coupled frequency could appear [9, 25]. Considering this fact, in the analysis of reflectivity spectra of Co doped PbTe we have decided to use dielectric function that takes into account the existence of free carriers – phonon interaction in advance [17]:

$$\varepsilon(\omega) = \varepsilon_{\infty} \frac{\prod_{j=1}^2 (\omega^2 + i\gamma_{lj}\omega - \omega_{lj}^2) \cdot \prod_{k=1}^n (\omega^2 + i\gamma_{Lk}\omega - \omega_{Lk}^2)}{\omega^{n+1} (\omega + i\gamma_p) (\omega^2 + i\gamma_l\omega - \omega_l^2) \prod_{k=1}^n (\omega^2 + i\gamma_{Ok}\omega - \omega_{Ok}^2)} \frac{\prod_{s=1}^s (\omega^2 + i\gamma_{LOm}\omega - \omega_{LOm}^2)}{\prod_{m=1}^m (\omega^2 + i\gamma_{TOm}\omega - \omega_{TOm}^2)} \quad (3)$$

In our case n is number of local phonons. The first term in Eq. 3 represents the coupling of one plasmon and $n + 1$ phonons, and second term represents the uncoupled modes of the crystal (s), while $l = n + s + 1$. The first term in Eq. 3 consist of two parts. The ω_{lj} ($j = 1, 2$) and ω_l represents plasma (γ_p is damping) and PbTe LO phonon mode interaction. The second part of this term represents interaction between plasma and cobalt local phonons, where the ω_{lk} ($k = 1, n$) is local phonon characteristic frequencies and ω_{Lk} is coupled frequency; γ_{Ok} and γ_{Lk} are the damping. The second term represents uncoupled crystal modes, where the ω_{LOm} and ω_{TOm} are the longitudinal and transverse uncoupled modes frequencies, while γ_{LOm} and γ_{TOm} are damping.

The justification to use mentioned type of dielectric function is demonstrated by performing the following analysis.

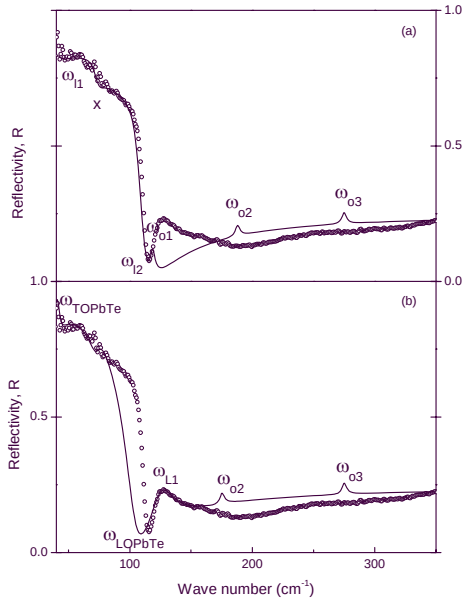


Fig. 1. Far – infrared reflection spectrum of the PbTe(Co) with Co concentration of 4×10^{19} at./cm³ at the temperature of 80 K. Circles – experimental data; Solid line – calculated spectra obtained by a fitting procedure based on the model for plasmon – phonon coupling: a) plasmon – LO_{PbTe} phonon coupling and b) plasmon – Co local phonon coupling.

The far – infrared reflection spectrum of the PbTe(Co) with Co concentration of 4×10^{19} at./cm³ at the temperature $T = 80$ K is presented in the Fig. 1 (a) and (b). The experimental data are presented by circles, while the solid lines represent the calculated spectrum obtained by a fitting procedure based on the model for plasmon – phonon coupling (see Eq. 3). The phonon structure of this sample consists of PbTe TO/LO phonon pairs, and three local phonon of Co, which will be discussed later. In the first case we assumed that PbTe origin TO/LO pair interacts with plasma (Fig. 1 (a)) and none of the three local phonons. We get the good overlapping of experimental and theoretical spectra only in interaction range. The similar situation is in the case when one Co local phonon (coupled frequency is denoted by ω_{L1}) interacts with plasma and PbTe origin TO/LO pair and other Co modes (ω_{o2} and ω_{o3}) do not (Fig. 1.b). Similar results will be obtained in the case when only Co modes ω_{o2} and ω_{o3} participates in the interaction. Mode at about 73 cm^{-1} denoted with x, is well known PbTe Brillouin zone edge mode [24].

As second possible case, we took that PbTe TO/LO pair and one local Co phonon (ω_{o1}) interacts with plasmon, while other local phonons (ω_{o2} and ω_{o3}) do not. This situation is shown in Fig. 2. The solid line is the calculated spectra obtained by a fitting procedure based on the model given by Eq. 3 ($n = 1, s = 3$). As one can see from the figure, the model agrees well with the experimental curve

for frequencies lower than 125 cm^{-1} , but it diverges from the experimental results at higher frequencies.

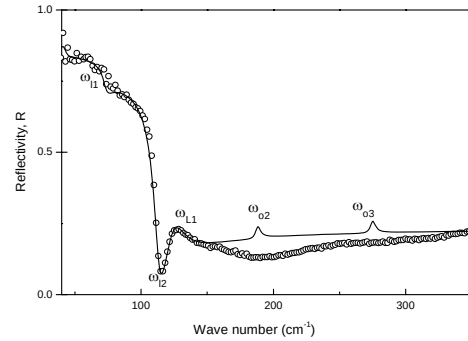


Fig. 2. Far – infrared reflection spectrum of the PbTe(Co) with Co concentration of 4×10^{19} at./cm³ at the temperature of 80 K. Circles – the experimental data, solid line – calculated spectra obtained by a fitting procedure based on the model for plasmon – phonon coupling (Eq. 3) where $n = 1$ and $s = 3$.

In the third case, we took that PbTe TO/LO pair and two local Co phonons (ω_{o1} and ω_{o2}) interact with plasmon, while third local phonon (ω_{o3}) does not (Fig. 3). In this case the solid line is obtained by a fitting procedure based on the model given by Eq. 3 where $n = 2$ and $s = 2$. The model agrees well with the experimental curve for frequencies lower than 270 cm^{-1} , but it diverges from the experimental results at higher frequencies. We did not succeed to determinate the set of parameters that provide good spectrum overlapping in the whole range of frequencies that corresponds to the parameters calculated from the suggested model at the same time. Finally, if we use the model that includes plasma interaction with PbTe TO/LO pair and three Co local phonon ($n = 3, s = 1$ in Eq. 3), we obtain good agreement with experimental results (see Fig. 4).

Based on the conducted analysis, it can be concluded that in analysis of the FIR reflection spectra of PbTe(Co), the dielectric function which will take into account the interaction of free carriers with PbTe TO / LO pair, and with all three local phonons Co, must be used.

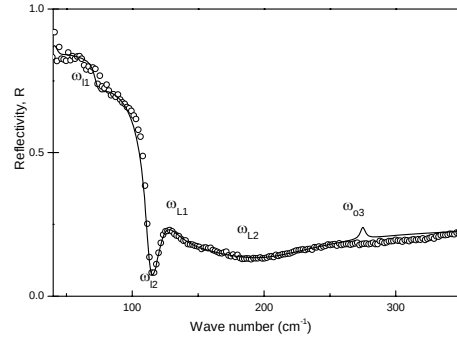


Fig. 3. Far – infrared reflection spectrum of the PbTe(Co) with Co concentration of 4×10^{19} at./cm³ at the temperature of 80 K. Circles – the experimental data, solid line – calculated spectra obtained by a fitting procedure based on the model for plasmon – phonon coupling (Eq. 3) where $n = 2$ and $s = 2$.

The parameters adjustment was carried out automatically, by means of the least – square fitting of theoretical (R) and experimental (R_e) reflection coefficients at q arbitrarily taken points:

$$\sigma = \sqrt{\frac{1}{q} \sum_{j=1}^q (R_{ej} - R_j)^2}, \quad (4)$$

where:

$$R = \left| \frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1} \right|^2 \quad (5)$$

and ε is given by Eq. 3. The value of σ was minimized until it became comparable with the usual experimental error (less than 2%). The cross-sections of multi-dimensional $\sigma(\omega, \gamma)$ surface were calculated, multiplying each parameter alternately by a varying factor ($1 \pm \delta$) while all the others were fixed on a determined level. Such sections gave evidence of the precision of the analyses. Practically, the determination errors of the eigenfrequencies and damping coefficients were in the range of 3 – 6 % and 10 – 15 %, respectively.

4. Results and discussion

The far – infrared reflection spectra of PbTe(Co) with Co concentration of and $4 \cdot 10^{19}$ at./cm³ single crystal in the temperature range from 80 to 300 K, and spectral range from 40 – 450 cm⁻¹ are shown in Fig. 4. The experimental data are marked by circles. The solid line was obtained using the dielectric function from Eq. 3, where $n = 3$ and $s = 1$. This means that Co existed in the three valence states, which means that there are three Co local phonons participating in the interaction.

Theoretical spectra fit experimental results very well. The characteristic parameters obtained as a best fit are shown in Fig. 5. The obtained results can be explained in the following way:

First of all, we shall examine the characteristic frequencies of the Co local phonons. Co in PbTe substitutes the Pb, and Co is a substitution impurity ion. The impurity mode can arise simply due to the difference between masses and force constants of the impurity ion and the ion of the host material [25], or their appearance can be caused by more complex mechanism of electron – phonon interaction [15, 16, 26]. In our case, taking into account the change of mass and force constants between an impurity and its surrounding, we have demonstrated that this is the case of the Co impurity local modes. That is, if the semiconductor is doped with a substitution impurity [25] (in this case Co), when substitution of the heavier mass (Pb) is made by a lighter impurity, one gets two modes: a local mode situated above the optical band and a gap mode situated above the acoustic band but below the optical band of the host lattice. Co impurity modes are situated above the PbTe host optical band (Fig. 5), so they are local modes.

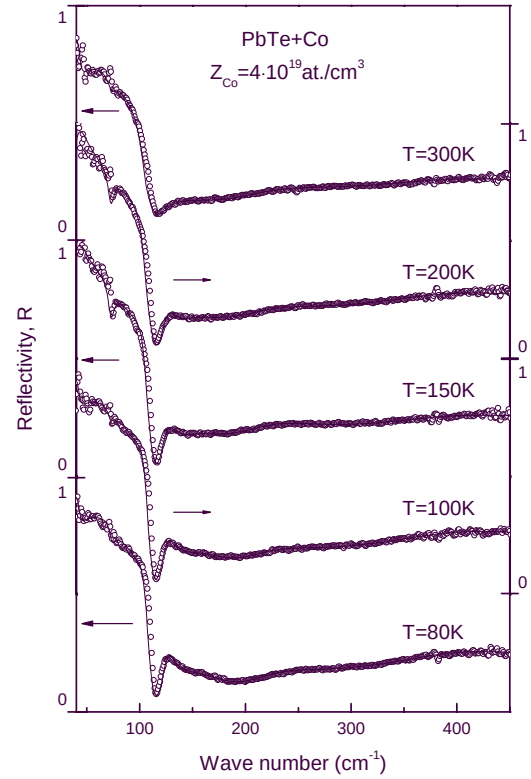


Fig. 4. Far – infrared reflection spectra of PbTe(Co) ($Z_{Co} = 4 \cdot 10^{19}$ at./cm³) single crystal in the temperature range from 80 to 300 K. Experimental spectra are presented by circles. Solid line is calculated spectra obtained by the fitting procedure based on the model for plasmon – phonon coupling (Eq. 3): $n = 3$, $s = 1$.

Taking into account, both the FIR and Hall measurements, we assume that in the case of very low concentration, Co enters PbTe lattice as electroneutral impurity in Co²⁺ state, similar as in the case of Mn doped PbTe. With further Co concentration increase, free concentration increase and we concluded that Co entered lattice as a Co²⁺ (as a neutral) and as a Co³⁺ (as a donor). Further Co concentration increasing produces free carrier concentration decrease and another local phonon, which corresponds to Co¹⁺ (acceptor state) occurs. The mentioned behaviour of Co causes strong correlation between an impurity center and a lattice. A change of the electronic state of an impurity centre provokes a change of the local mode frequency. According to these results we concluded that the mode at about 190 cm⁻¹ corresponded to Co²⁺, the mode at about 275 cm⁻¹ to Co³⁺, and the mode at 125 cm⁻¹ to Co¹⁺. As was reported in [27] those type of modes, due to ionisation, have positive frequency shift (in our case: +75 cm⁻¹: Co²⁺ – Co¹⁺; +160 cm⁻¹: Co³⁺ – Co¹⁺). These modes show significant coupling with charge carriers [27]. Hypothetical position of unionised Co local mode is at about 50 cm⁻¹. That is the zone where the density states in the PbTe have a minimum [28]. Such

place is very suitable for the formation of gap modes, as was the case with one of the Mn local modes [18].

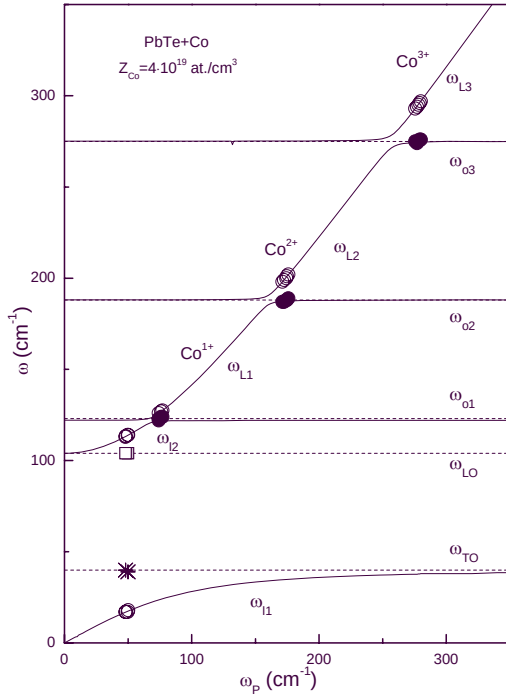


Fig. 5. The eigenfrequencies of the plasmon – phonon modes for single crystal PbTe(Co) with $Z_{Co}=4 \times 10^{19}$ at./cm³: the solid lines are calculated spectra [$\text{Re}\{\epsilon\}=0$; ϵ is given by Eq. 2, $l=4$]; ● – ω_{02} , ω_{03} , ω_{01} , ω_{L1} , ω_{L2} and ω_{L3} (Eq. 3); * – experimentally determined values for ω_{TO} , ω_{01} , ω_{02} and ω_{03} ; X – ω_{LOPbTe} . Dashed lines are visual aid.

In Fig. 5 characteristic spectra for plasmon – phonon interaction are presented. There is, interaction of one plasmon with PbTe TO/LO pair and three Co local phonon is presented. Obtained results should describe the relationship between the results obtained on the basis of Eq. 3 and of the traditional approach presented with Eq. 2. The solid line, represents coupled frequencies, and as it was given in [17] the positions of the coupled mode were defined as the solutions of Eq. 2 ($\text{Re}\{\epsilon\} = 0$). Dashed lines, obtained experimentally as the best fit, correspond to TO phonon positions, Co local phonon characteristic frequencies (ω_{0k} , $k=1, 3$) and well – known value for PbTe LO phonon [6]. Positions of coupled frequencies, obtained as the best fit using the appropriate Eq. 3, are presented as symbols: the solid circles (●) refer to Co local frequencies and stars (*) to PbTe TO phonon. We presumed that PbTe phonons interact with plasma only, e.g. this interaction is not influenced by impurity centers directly. Therefore, we can determine the value of the LO phonon and the plasma frequency, as described in Ref. 18.

Since the calculated value for the LO phonon coincides with the values from the literature, we conclude that this approach was justified. If we followed the described procedure for the local phonons of Co also, e.g. if we join positions of the coupled phonons with, by this manner, calculated plasma, we would obtain large difference for values of coupled frequencies calculated from Eq. 2 and Eq. 3. That is the reason why we positioned coupled frequencies on the theoretical curves, and then we read the value of the plasma frequency. We observe linear shift of the plasma frequency values when the ionisation state of the impurity center increases. In other words saying, the successive impurity center ionisation leads to the characteristic positive frequency shift. Hereby, the interaction between ionised center and the free carriers becomes stronger. One of the mechanisms that can describe this situation is related with changes of the density of the free carriers in the vicinity of the ionised center [12]. Besides, it is possible that near ionised centre different plasma modes are formed. In former case, the Coulomb interaction of different plasma modes forms in the limits of one energy band the single collective excitation, which is displayed in our spectra with an eigenfrequency equal to

$$\omega_P = \left[\sum_{j=1}^m \omega_{jP}^2 \right]^{1/2} \quad (6)$$

Assume that in this case free carriers are in a some way tied to close neighbourhood around the charged impurity center. Also, we shall assume that here we have a two – component plasma around each impurity center, where one component is determined from PbTe coupling.

Obtained results should be understood only qualitatively. Namely, noticed plasmon – ionised impurity – phonon interaction can be described in several manners [see for example Refs. 9, 15, 16, 23, 25]. However, in all cases the increase in the amount of interaction must be observed, while the ionisation state of the impurity center increases, as well as its local character.

Doping PbTe by Co causes appearance of paramagnetic properties. Magnetic measurements is obtained paramagnetic (or ferromagnetic) signal that does not depends on temperature (Fig. 6). It suggest that besides Co inclusions (Curie temperature 1400K) there are some inclusion of cobalt compounds like CoTe_x , where is x molar content of tellurium. Namely, increase in tellurium content decreases the saturation moment of this compound, and when x is less than 1.2, the compound is no longer ferromagnetic but shows a feeble constant paramagnetic which is independent of temperature [29].

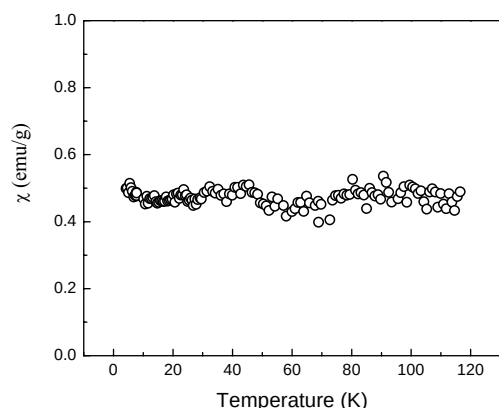


Fig. 6. Magnetic susceptibility of PbTe(Co).

5. Conclusions

As a method to investigate phonon properties of Co doped PbTe ($Z_{\text{Co}} = 4 \times 10^{19} \text{ at./cm}^3$) single crystal we used far – infrared spectroscopy. We obtained three local modes of Co at about 125, 190 and 275 cm^{-1} , which corresponded to the impurity atoms in different valence states. The positions of these modes depend on impurity centre charge. We also revealed that in this system plasmon – ionised impurity – phonon coupling existed. Magnetic measurements show the appearance of paramagnetic properties at PbTe alloy doped with Co.

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