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Magneto-optical effects in $Bi_{1-x}As_x$ with $x = 0.01$: Comparison with topological insulator $Bi_{1-x}Sb_x$ with $x = 0.20$

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In this work, we explore possible topological insulating state in bismuth doped with arsenic $Bi_{1-x}As_x$. Infrared and magneto-optical spectroscopy are employed to probe the electrodynamic response of $Bi_{1-x}As_x$ with $x = 0.01$, as well as topological insulator $Bi_{1-x}Sb_x$ with $x = 0.20$. The spectra are reported in magnetic fields up to 18 T, and at temperatures between 10 and 300 K. The results indicate strong sensitivity of optical properties to these external stimuli in both $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$, but also some differences introduced by arsenic doping. Most notably, the field dependence of cyclotron resonance in $Bi_{1-x}As_x$ implies that it is due to bulk carriers, as opposed to surface carriers in $Bi_{1-x}Sb_x$.

1 Introduction Topological insulators (TI) are currently at the focus of condensed matter research [1–3]. Particularly interesting are 3D TI, such as Bi_2Se_3, Bi_2Te_3, and $Bi_{1-x}Sb_x$, which have been predicted theoretically and experimentally confirmed to have Dirac electrons on their surfaces [4, 5]. These Dirac electrons are also topologically protected from back-scattering on non-magnetic impurities [1, 2, 6]. The search for new TI is based mostly on bismuth (Bi) and its compounds. Electronic structure of semi-metallic Bi is strongly affected by doping. For example, when doped with antimony (Sb), the semi-metallic character of Bi is suppressed and its band structure gradually evolves caused by strong spin–orbit coupling. For doping levels $0.07 < x < 0.22$ $Bi_{1-x}Sb_x$ is a topological insulator [1, 2].

In this work, we explore the possibility of realizing TI state in Bi doped with arsenic (As), instead of Sb. Arsenic and antimony are in the same group of the periodic table, and it is not unreasonable to expect that similar growth conditions could be used, and more importantly that the two systems would have similar electronic properties. We employ far-infrared and magneto-optical spectroscopies to study the properties of $Bi_{1-x}As_x$ with $x = 0.01$, as well as $Bi_{1-x}Sb_x$ with $x = 0.20$ [7]. In the past few decades, infrared (IR) and magneto-optical spectroscopies have been used for studies of a wide array of materials [8–10]. Recently, they have also been used extensively for studies of TI [11–15]. The results presented here on $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$ reveal that both dopants have similar effect on the infrared and magneto-optical spectra. However, we also find that one of magneto-optical modes has different field dependence in the two systems, which indicates that its nature is different.

2 Experimental results $Bi_{1-x}Sb_x$ and $Bi_{1-x}As_x$ samples were grown at the Serbian Academy of Sciences and Arts, as described previously [16]. For spectroscopic measurements, the samples were mechanically polished, to achieve optically flat surfaces. Far-IR measurements were

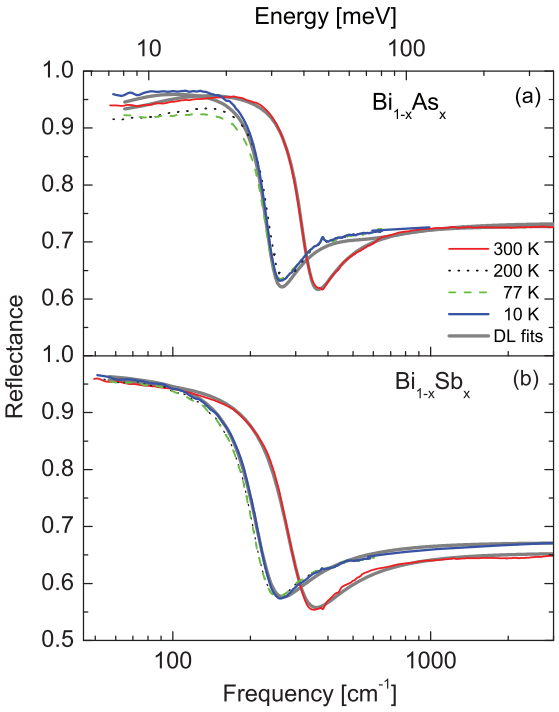

Figure 1 (a) Zero-field reflectance spectra of $Bi_{1-x}As_x$ with $x = 0.01$, at 10, 77, 200, and 300 K. Gray lines represent Drude fits (Eq. (1)) of reflectance at 10 and 300 K. (b) Reflectance spectra of $Bi_{1-x}Sb_x$ with $x = 0.20$ in zero magnetic fields at the same temperatures as for $Bi_{1-x}As_x$.

performed at The University of Akron, using overcoating technique [17]. Magneto-optical measurements were carried out at the National High Magnetic Field Laboratory (NHMFL). The reflectance ratios $R(B)/R(0\,\mathrm{T})$ measured at NHMFL were supplemented with the absolute values of reflectance in zero field, to obtain the absolute values of reflectance in magnetic field $R(\omega, B)$ [18].

Figure 1 shows the far-infrared reflectance of both $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$ at selected temperatures. Overall, these spectra look similar to the IR spectra of other studied TIs, such as Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 [11, 15]. They are all dominated by a characteristic plasma edge due to free charge carriers. In $Bi_{1-x}As_x$, the plasma minimum is located at 375 cm^{-1} at 300 K, and as temperature decreases to 200 K it shifts to 265 cm^{-1}, but stays at approximately the same frequency down to 10 K. In $Bi_{1-x}Sb_x$, the plasma minimum is located at 355 cm^{-1} at 300 K, and as temperature decreases it shifts to 265 cm^{-1} at 200 K. Similar to $Bi_{1-x}As_x$, below 200 K, the plasma minimum shows little temperature dependence. The plasmaron mode, which in the spectra of pure Bi appears as a sharp mode at frequencies slightly above the plasma minimum [19, 20], is suppressed by doping in both $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$. We were able to obtain satisfactory fits of experimental data using a conventional

Table 1 Parameters of Drude fits from Eq. (1). Plasma frequencies $\omega_{p,i}$ and scattering rates γ_i are shown for both $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$, at 10 and 300 K. All values are in cm^{-1}.

	$Bi_{1-x}As_x$		$Bi_{1-x}Sb_x$	
	300 K	10 K	300 K	10 K
$\omega_{p,1}$	4400	3110	2790	2250
γ_1	58	17	61	36
$\omega_{p,2}$	4220	4800	2755	3540
γ_2	2160	2200	1090	2120

Drude model [8–10]:

$$\varepsilon(\omega) = \varepsilon_\infty - \sum_i \frac{\omega_{p,i}^2}{\omega(\omega + i\gamma_i)}. \quad (1)$$

In Eq. (1), ε_∞ is the high-frequency dielectric constant, $\omega_{p,i}$ plasma frequency and γ_i scattering rate. A minimum of two Drude modes ($i = 1, 2$) was necessary to achieve satisfactory fits. Bi and $Bi_{1-x}Sb_x$ have been known to have both electrons and holes present [21, 22], which can be phenomenologically assigned to two Drude modes. The spectra in Fig. 1, combined with the fits (Eq. (1)) indicate that $Bi_{1-x}As_x$ probably also has two types of charge carriers. The values of fitting parameters from Eq. (1) are reported in Table 1.

In magnetic field both samples display strong magneto-optical activity, as indicated by Fig. 2, which displays the absolute values of reflectance at different fields and at 10 K. The effect of magnetic field on reflectance is stronger in $Bi_{1-x}As_x$, where a so-called "second plasma edge" can clearly be observed in highest magnetic fields. We also note large field induced changes in reflectance at the lowest measured frequencies, where the reflectance shows characteristic downturn. Similar, but weaker field effects can also be identified in the spectra of $Bi_{1-x}Sb_x$, as well as in pure bismuth [20].

3 Discussion To better understand electrodynamic properties of $Bi_{1-x}As_x$, we extract other optical functions from reflectance. We fit the spectra and from the best fits obtain the dielectric function tensor $\varepsilon_\pm(\omega) = \varepsilon_{xx} \pm i\varepsilon_{xy}$, where plus and minus components correspond to right and left circular polarizations. Drude–Lorentz model is employed, with the addition of a cyclotron term [23]. With this modification $\varepsilon_\pm(\omega)$ is:

$$\varepsilon_\pm(\omega) = \varepsilon_\infty + \sum_i \frac{\omega_{p,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_i\omega \mp \omega_{c,i}\omega}. \quad (2)$$

In Eq. (2) $\omega_{c,i}$ is the cyclotron frequency, $\omega_{0,i}$ is the frequency of the mode, and $\omega_{p,i}$, γ_i are the same as in Eq. (1). The cyclotron frequency is usually taken as positive for electron-like and negative for hole-like carriers. One can easily verify that Eq. (2) equivalent to Eq. (1) in the limit $\omega_0 = 0$ and $\omega_c = 0$. The fitting of experimental spectra was done with

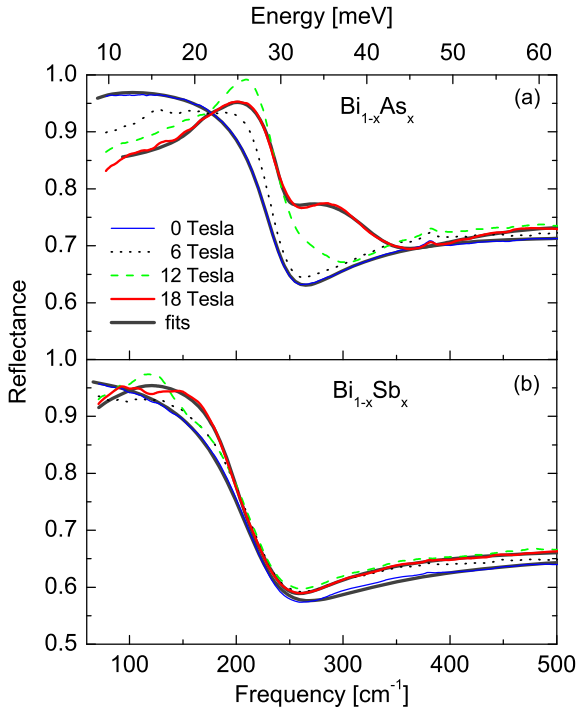

Figure 2 (a) Reflectance spectra of $Bi_{1-x}As_x$ with $x = 0.01$ in magnetic field at several different field points and at 10 K. Also shown with gray lines are the fits of reflectance at 0 and 18 T, obtained from Eq. (2). (b) Reflectance spectra of $Bi_{1-x}Sb_x$ in magnetic fields at several magnetic field values.

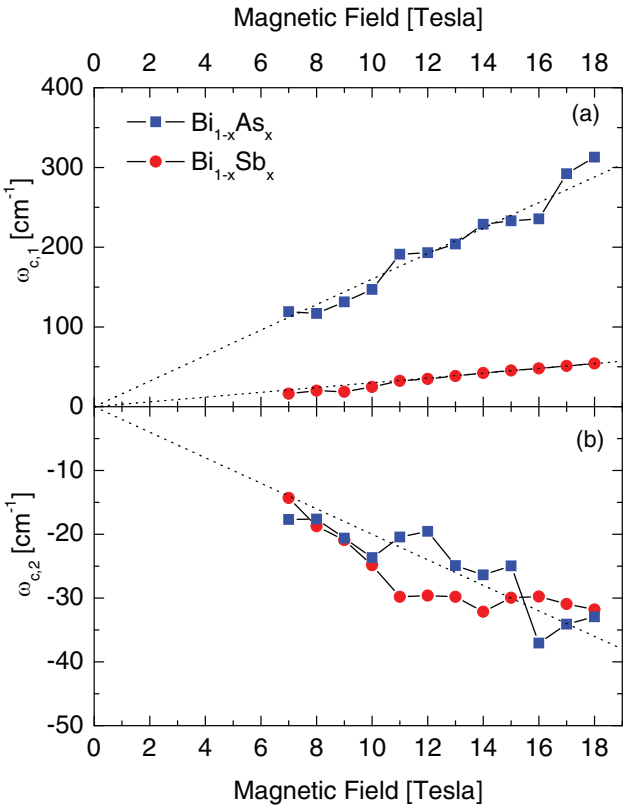

Figure 3 Cyclotron frequencies of both modes obtained from the fits of reflectance (Eq. (2)). The modes are outside of our measured frequency window ($\omega > 50\,\mathrm{cm}^{-1}$) below about 7 T which renders the fits less reliable, and they are not shown. Above 7 T, the results indicate that one cyclotron mode has similar values in both samples, whereas the other one is at higher energy in $Bi_{1-x}As_x$. Dashed lines are guides for the eye.

RefFIT [24]. For both samples Eq. (2) is used with two modes ($i = 1, 2$), but with opposite signs of their cyclotron frequencies ($\omega_{c,1}$ and $\omega_{c,2}$). The results for 0 and 18 T are shown in Fig. 2 with gray lines.

The values of cyclotron frequencies $\omega_{c,1}$ and $\omega_{c,2}$ from Eq. (2) are shown in Fig. 3 for both compounds. There are two cyclotron modes, one for each type of charge carriers, and their cyclotron frequencies $\omega_{c,1}$ and $\omega_{c,2}$ have the opposite signs. This is consistent with the presence of two types of charge carriers, as inferred above based on the spectra in zero field. As can be seen from Fig. 3 both $\omega_{c,1}$ and $|\omega_{c,2}|$ increase approximately as linear functions of the field. The values of $\omega_{c,2}$ are relatively small and have larger error bars associated with them. We also note that $\omega_{c,2}$ has similar values for both compounds, whereas $\omega_{c,1}$ is substantially larger in $Bi_{1-x}As_x$ compared with $Bi_{1-x}Sb_x$.

The fitting procedure presented above (Figs. 2 and 3) suggests that charge dynamics in the two studied systems is similar. However, there are some differences between them (e.g., $\omega_{c,1}$ is several times bigger in $Bi_{1-x}As_x$) that we now explore further. An alternative approach of analyzing magneto-optics data was recently proposed by Schafgans et al. [14]. Their procedure is model-independent and consists of plotting the derivative of reflectance with respect to magnetic field, $\mathrm{d}R(\omega,B)/\mathrm{d}B$. This method has been shown to be a very sensitive tool for identification of modes in magneto-optical spectra [14]. In Fig. 4, we plot the derivative spectra $\mathrm{d}R(\omega,B)/\mathrm{d}B$ for both compounds, and indeed there are notable differences between $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$.

Both spectra are dominated by a strong mode with a positive slope (red regions) that disperses with magnetic field up to 18 T. We point out that the observed features *are not* due to the plasma minimum, whose zero-field values are marked with the arrow for both compounds. The mode is significantly narrower in $Bi_{1-x}Sb_x$ compared with $Bi_{1-x}As_x$. However, the most important difference between the two is the behavior of this mode at low fields. Namely, in $Bi_{1-x}Sb_x$ the mode extrapolates to zero frequency at $B = 0$ T [25], whereas in $Bi_{1-x}As_x$ it clearly extrapolates to a finite value ($130\,\mathrm{cm}^{-1}$).

According to theoretical analysis of Schafgans et al. [14] this indicates that the nature of the modes is different. Namely, in TI the response to external magnetic field, especially at low fields, is different for bulk and surface modes. Modes involving bulk carriers always extrapolate to finite frequencies for $B \to 0$, as a linear function of the field. On the other hand, electronic transition involing surface carriers extrapolate to zero frequency for $B \to 0$, and for low fields

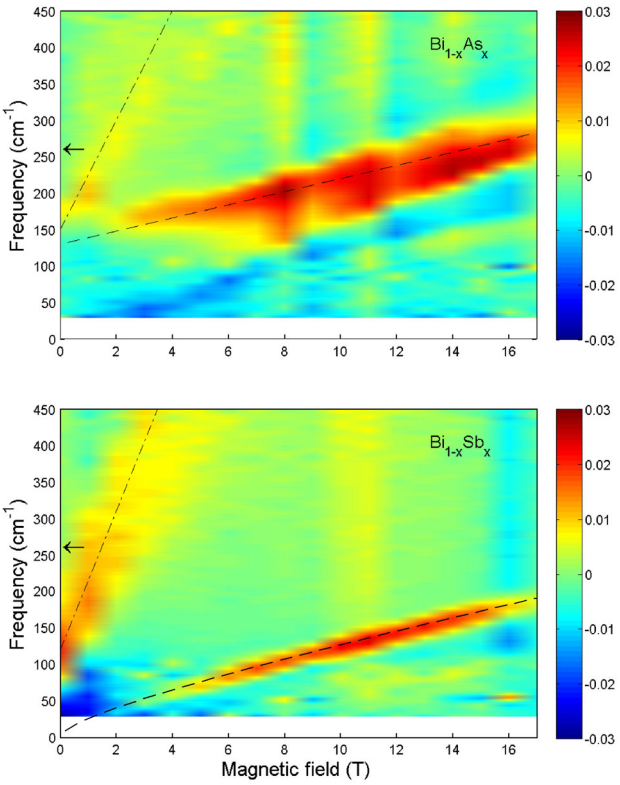

Figure 4 Reflectance derivative maps $dR(\omega,B)/dB$ are shown for both samples. Dashed and dash-dotted lines are the fits explained in the text. The arrows point to the position of zero-field plasma minimum.

their field dependence is proportional to $\sqrt{B}$, which gradually becomes linear at higher fields. This analysis implies that the mode in $Bi_{1-x}Sb_x$ is a surface state mode, whereas the one in $Bi_{1-x}As_x$ is a bulk mode. The best fit, shown with a dashed line in Fig. 4, yields for the surface mode in $Bi_{1-x}Sb_x$ $\omega_c(B) = 6.4B + 20\sqrt{B}$. On the other, the fit of the mode in $Bi_{1-x}Sb_x$ is $\omega_c(B)$= 130 + 9B, with negligible $\sqrt{B}$ contribution.

Close inspection of Fig. 4 also reveals that in addition to these two strong modes, two weaker modes are also present, marked with dash-dotted lines. They are approximately linear functions of the field and both extrapolate to finite frequencies. The best fits yield $\omega_c(B) = 150 + 75B$ for $Bi_{1-x}As_x$ and $\omega_c(B) = 120 + 95B$ for $Bi_{1-x}Sb_x$. We assign both modes to bulk cyclotron modes and extract values of the bulk gaps of 150 and 120 cm^{-1} in $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$, respectively. These values are smaller than the gap value for $Bi_{1-x}Sb_x$ with $x = 0.09$, extracted from optical conductivity (385 cm^{-1}) [14].

4 Summary In search of possible topological insulating state in $Bi_{1-x}As_x$ with $x = 0.01$, we studied its optical and magneto-optical properties in magnetic fields up to 18 T, and compared them with the corresponding spectra of $Bi_{1-x}Sb_x$ with $x = 0.20$. We found that, even though their spectra look similar, $Bi_{1-x}As_x$ and $Bi_{1-x}Sb_x$ are different. Most notably, the strongest mode in the spectra appears to be a surface state mode in $Bi_{1-x}Sb_x$, whereas in $Bi_{1-x}As_x$ it seems to be a bulk mode. In spite of that, our results indicate that charge dynamics of $Bi_{1-x}As_x$ is worth exploring further, especially with spin-sensitive techniques [26].

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[25] One can also argue that the mode extrapolates to a small finite value. Based on our frequency window ($\omega > 50\,\mathrm{cm}^{-1}$), we cannot exclude that possibility.
[26] In addition to surface states with linear (Dirac) dispersion, the bulk valence band in $Bi_{1-x}Sb_x$ has also been found to be linear using ARPES [4]. We susspect that might also be the case in $Bi_{1-x}As_x$.

