Infrared Spectroscopy of the Topological Surface States of Bi_{2}Se_{3} by Use of the Berreman Effect

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Infrared spectroscopy of the topological surface states of Bi_2Se_3 by use of the Berreman effect

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Abstract

The Berreman effect (BE) allows one to study the electrodynamics of ultrathin conducting films at the surface of dielectrics by use of grazing-angle infrared spectroscopy and polarized radiation. Here, we have first applied the BE to the two-dimensional electron system (2DES) at the interface between a high-purity film of the topological insulator Bi_2Se_3 and its sapphire substrate. We have determined for the 2DES a charge density $n_s = (8 \pm 1) \times 10^{12}$ cm^{-2}, a thickness $d = 0.6 \pm 0.2$ nm and a mobility $\mu^{IR} = 290 \pm 30$ cm^2/Vs. Within errors, all these parameters result to be independent of temperature between 300 and 10 K. These findings consistently indicate that the 2DES is formed by topological surface states, whose infrared response has then been directly observed here.

PACS numbers:

An ideally pure Bi_2Se_3 single crystal or thin film is a three-dimensional topological Insulator (TI) where a two-dimensional electron system (2DES) forms spontaneously at the interface with another dielectric due to the peculiar topology of the TI electronic bands, which are dominated by strong spin-orbit effects[1–3]. The topological surface states (TSS) in the 2DES are protected from back-scattering by a strong coupling between spin and momentum, so that their mobility is remarkably high, and virtually constant up to room temperature[4]. However, in real samples, a finite amount of Se vacancies are always present. They provide free electrons at virtually all temperatures, due to the high permittivity ($\sim$ 110) and low effective mass ($m^* \simeq 0.20 m_e$) characteristic of Bi_2Se_3[5]. In order to match the bulk chemical potential with the Fermi energy[6] of the TSS, a band bending occurs at the TI surface, which may attract or repel part of those carriers. In the frequent occurrence of downward band bending, a charge-transfer (CT) process accumulates electrons from the bulk to the surface. Their density n_{CT} thus may add to the TSS density n_{TSS}, possibly obscuring the topological contribution to the surface electrodynamics. The thickness d of the surface carrier layer at the Bi_2Se_3 surface has been estimated to be between 3 and 1 nm[6–8], of the same order of magnitude as that which forms at the interface between $LaAlO_3$ and $SrTiO_3$[9,10], and then can be considered as a 2DES. Recently, thin films of Bi_2Se_3 deposited by Molecular Beam Epitaxy (MBE) on sapphire (Al_2O_3) substrates have displayed total charge densities very similar to those expected for a 2DES formed by TSS alone[6], demonstrating the high purity of the film. This result has allowed for a direct inspection of the 2DES in thin Bi_2Se_3 films by several experimental tools, including infrared spectroscopy (IRS). For example, IRS has been successfully used to detect the 2DES plasmonic excitations in lithographically patterned Bi_2Se_3 films[11,12].

In Bi_2Se_3 thin films, one 2DES forms at the film-vacuum interface, and another one at the film-substrate interface. Here we use IRS to study the electrodynamics of the 2DES at the TI/sapphire interface, by exploiting the Berreman effect (BE)[13]. This technique allows one to detect the longitudinal excitations of ultrathin polar systems, such as vibrations of adsorbed layers or the Drude absorption of 2D free-electron systems. For instance, it has been successfully employed to measure in a non-contact mode the conducting properties of the quasi-2DES at the $LaAlO_3/SrTiO_3$ interface[10,14,15], a few nanometers thick. The BE exploits the strong electric dipole that the component of the radiation electric field in the plane of incidence (p-component) creates when entering a film of thickness d much smaller

than both the radiation wavelength λ and the field penetration depth d_p. For a conducting layer at the interface between two dielectrics, as in $LaAlO_3/SrTiO_3$ or here in Bi_2Se_3/Al_2O_3, a BE resonance is expected to appear at a radiation frequency ω such that the real part $\epsilon_1(\omega)$ of the dielectric function $\tilde{\epsilon}(\omega)$ of either dielectric is zero. As the only strong optical phonon of Bi_2Se_3 (α mode) falls in the THz range[16], one here may look for the BE at the strong and narrow LO phonons of the substrate, similarly to what done for detecting the BE at the interface $LaAlO_3/SrTiO_3$[10,14,15] with a strong phonon of $SrTiO_3$. One may notice that the observation of the BE due to the 2DES is insensitive to the fact that the longitudinal optical phonon oscillation takes place in the material hosting the interfacial 2DES (STO in the case of the LAO/STO) or in the substrate in close contact with the 2DES (sapphire in the present case).

The BE resonance is a very weak feature. Indeed, once the above conditions $d << \lambda$, $d << d_p$ are satisfied, its intensity decreases rapidly for $d \to 0$. The optimum thickness for the observation of an ultrathin layer by the Berreman effect is[17]

$$d_{opt} = (\lambda/2\pi)(cos\theta/sin^2\theta)\Xi_{max} \tag{1}$$

where θ is the angle of incidence and Ξ_{max} is the value at resonance of the energy loss function $\Xi = Im[-1/\tilde{\epsilon}]$. For example, in the quasi-2DES at a LAO/STO interface, d_{opt} is approximately[10] 50 nm, a value much larger than its actual thickness of a few nanometers. Even if our optics with a single polarizer do not implement an ellipsometric setup, it is useful to express the results in terms of the ellipsometric angle

$$\Psi(\omega) = \arctan[(R_p/R_s)^{1/2}] \tag{2}$$

where R_p (R_s) is the sample reflectivity in p (s) polarization. If moreover $\Psi_{film+sub}(\omega)$ is the angle measured on the TI/sapphire system and $\Psi_{sub}(\omega)$ is that of the bare sapphire substrate, separately measured, their difference

$$\Delta\Psi(\omega) = \Psi_{film+sub}(\omega) - \Psi_{sub}(\omega) \tag{3}$$

will show the typical Berreman feature made of a narrow dip followed by a broad peak at higher frequency, induced by the presence of the 2DES at the TI/sapphire interface. Indeed, the opposite 2DES at the TI/vacuum interface cannot contribute to the present observations

because its direct absorption - in the absence of BE - is vanishingly small in our frequency range. One can also exclude any electromagnetic interaction between the TSS at the two interfaces, as their distance (120 nm) is much larger than the range of such interaction[18]. By using Eq. 3 and polarized radiation at grazing incidence, we detected Berreman resonances at the reflectivity edges of two LO phonons of sapphire, at 391 and 482 cm^{-1} (at 300 K). Then, by using Fresnel formulas for the optical response of a multilayer[10,19], and Drude-Lorentz fits, we extracted from the spectra the parameters of the 2DES. We could thus collect strong indications that the observed conducting layer is indeed formed by topological surface states.

High-quality Bi_2Se_3 thin films, 120 nm thick, were prepared by molecular beam epitaxy using the standard two-step growth method developed at the Rutgers University[8,20]. The 10 $\times$ 10 mm^2 Al_2O_3 substrates were first cleaned by heating to 750 °C in an oxygen environment to remove organic surface contamination. The substrates were then cooled to 170 °C, and an initial set of three quintuple layers of Bi_2Se_3 was deposited. This was followed by heating to 300 °C, at which the remainder of the film was deposited to achieve the target thickness. The Se:Bi flux ratio was kept to 10:1 to minimize Se vacancies.

The reflectances R_p and R_s, (in p and s polarization, respectively) of the bare sapphire substrate and of the TI/sapphire system were measured under an angle of incidence $\theta = 72°$, by combining a Bruker IFS125 HR interferometer with the infrared synchrotron radiation source of the AILES beamline at the SOLEIL storage ring[21,22]. The interferometer was equipped with a 6 microns beamsplitter and with a Bolometer from IR Labs. The spectra resulted from averaging 300 scans recorded at 80 kHz with 2 cm^{-1} resolution. The samples were thermoregulated within $\pm$ 1 K by means of a closed-cycle He cryostat from CryoMec. A gold mirror placed at the same position as the sample, and aligned parallel to it by a laser beam, was used as reference. A single polyethilene polarizer, that could be remotely rotated, was placed on the radiation path. The optics of the interferometer limited the energy of the incident radiation below 1000 cm^{-1}, a value lower than the band gap of Bi_2Se_3[16], thus preventing its possible photodoping. The reflectances R_p and R_s thus obtained on the Bi_2Se_3 film deposited on Al_2O_3, and on the bare sapphire substrate, are shown in panels a and b of Fig. 1, respectively. Spectra in b are fully consistent with the reflectivity of sapphire at high angle of incidence reported in the literature[23,24].

The solid lines in Figure 2 show the ellipsometric angle Ψ from Eq. 2 at three temper-

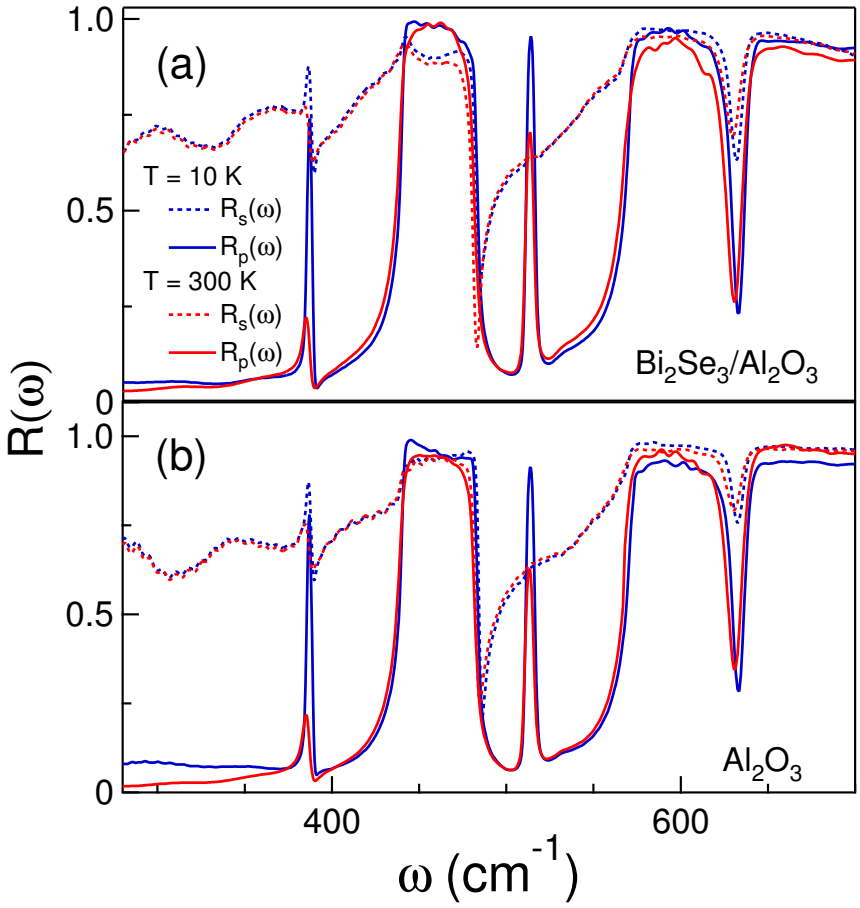

FIG. 1: Reflectivity in p and s polarization, at two temperatures, of a Bi_2Se_3 film on Al_2O_3 (a) and of a bare Al_2O_3 substrate (b).

atures, in the region of the LO1 and LO2 longitudinal phonons of sapphire peaked (at 300 K) at 391 and 482 cm^{-1}, respectively, as obtained from Eq. 2 applied to the spectra in Fig. 1. Thanks to the excellent signal-to-noise ratio achieved by infrared SR we could detect the reproducible differences $\Delta\Psi(\omega) = \Psi_{film+sub}(\omega) - \Psi_{sub}(\omega)$ plotted in Fig. 3. Therein, $\Delta\Psi(\omega)$ shows at all temperatures the expected Berreman resonance formed by a dip followed by a broad peak at higher frequency. The fluctuations with temperature of the dip broadening have no physical meaning[25], while the dip depth is related to the plasma frequency of the conducting layer[10], and then to the 2DES charge density N. The peak also provides a measurement of the carrier relaxation rate Γ_D. As one can see, the dip amplitude (and then N)

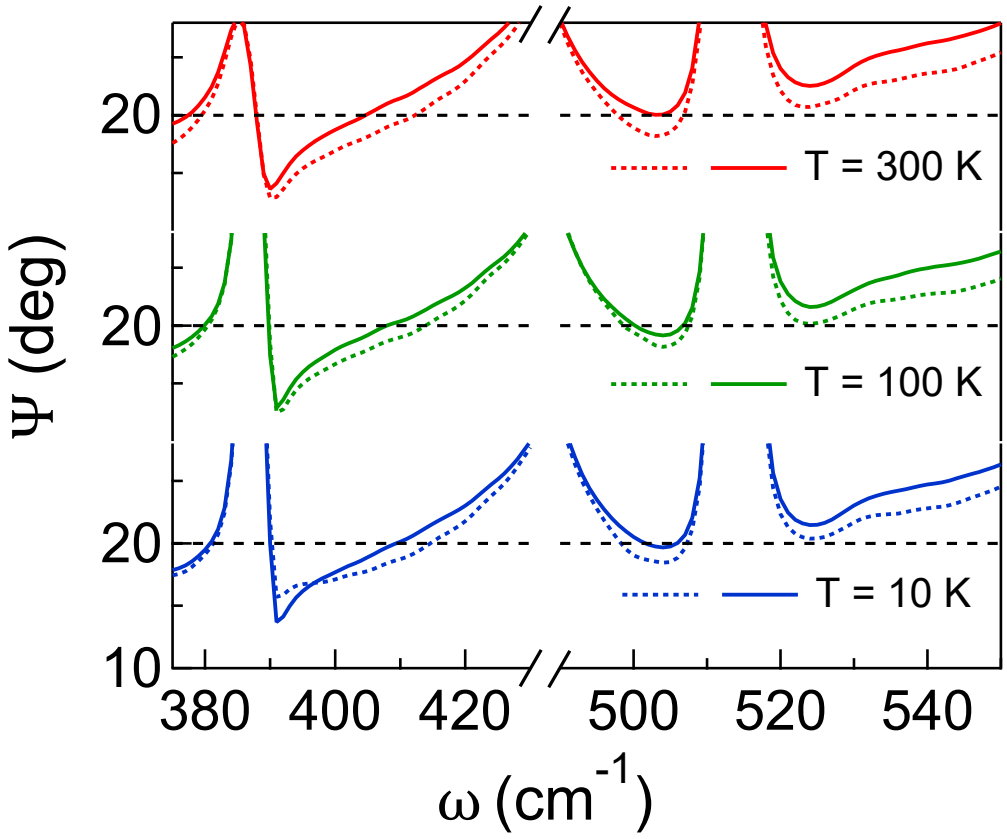

FIG. 2: Ellipsometric angles Ψ at three temperatures, from Eq. 2 and data in Fig. 1, in the region of the LO1 (a) and LO2 (b) phonons of sapphire. Solid lines refer to the TI/sapphire system, dotted lines to the bare sapphire substrate.

is basically independent of T, as expected for a metallic system. The curves in Fig. 3 were fit to the usual Fresnel equations[10,19] which relate the reflectivity of a multi-layer optical system, in both polarizations, to the dielectric function of the individual layers. Here the fit was applied to the present three-layer system made of i) a vacuum, which includes the bulk of the Bi_2Se_3 film which is transparent in the present frequency range; ii) a conducting ultrathin layer of Bi_2Se_3 having thickness d, plasma frequency ω_p, and relaxation rate Γ_D; iii) a seminfinite Al_2O_3 insulating substrate whose phonon spectrum is modeled by the Lyddane-Sachs-Teller dielectric function[26].

$$\widetilde{\epsilon_2}(\omega) = \epsilon_\infty \prod_j \frac{(\Omega_{Lj}^2) - \omega^2 + i(\Gamma_{Lj})\omega}{(\Omega_{Tj}^2) - \omega^2 + i(\Gamma_{Tj})\omega}. \quad (4)$$

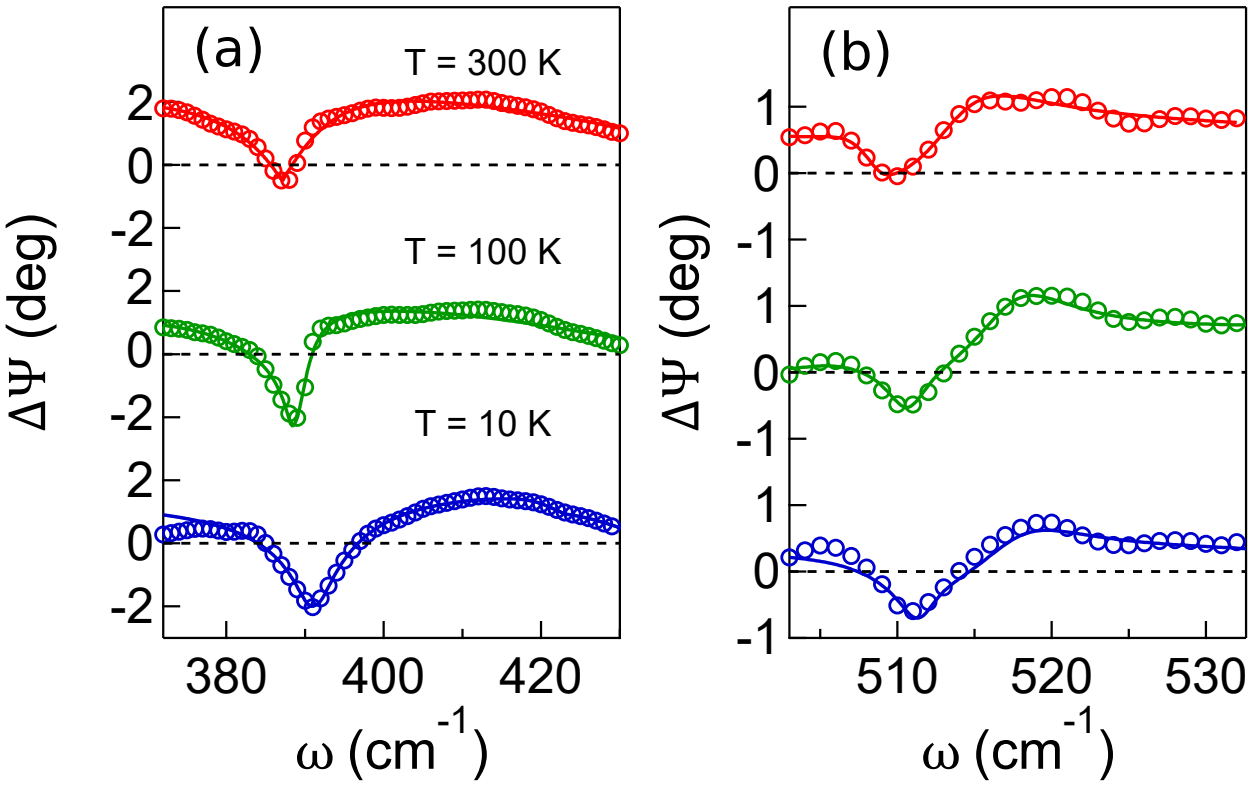

FIG. 3: Berreman resonances at the interface between Bi_2Se_3 and Al_2O_3, in the spectral regions of sapphire phonons LO1 (a) and LO2 (b), at three temperatures (circles). The solid lines are fitting curves obtained by the procedure described in the text.

Therein, ϵ_∞ is the contribution to the dielectric function from oscillators at energies higher than the phonon energies, Ω_{Lj} and Ω_{Tj} are the central frequencies of the longitudinal and transverse optical phonons, respectively, while Γ_{Lj} and Γ_{Tj} are the corresponding line widths. Details of the fitting procedure and an explanation of the assumptions we made are given in the Supplemental Information (SI)[27]. In Fig. 3, the fitting curves obtained by the above procedure are reported by solid lines. The resulting parameters of the Drude model for the conducting film are listed in Table I, together with those of the sapphire phonons LO1 and LO2 which trigger the resonance. As one may notice in the Table, all the fitting parameters of the conducting layer are scattered vs. temperature within a small interval that can be reasonably ascribed to the propagation of the experimental error. One can then average

TABLE I: Fitting parameters for the 2DES at the interface between Bi_2Se_3 and Al_2O_3, as obtained from the Berreman resonances at LO1 and LO2 shown in Fig. 3. The 2DES thickness d is in nm. All the other values (2DES plasma frequencies ω_p and relaxation rates Γ_D, sapphire longitudinal phonon frequencies ω_{LO} and widths Γ_{LO}) are in cm^{-1}. The parameters indexed 1 (2) were extracted from the Berreman resonance at the sapphire longitudinal phonons LO1 (LO2). All phonon parameters of the sapphire substrate, as obtained from the fit to its reflectivity, are reported in Table I of the SI[27].

T (K)	d_1	ω_{p1}	Γ_{D1}	ω_{LO1}	Γ_{LO1}	d_2	ω_{p2}	Γ_{D2}	ω_{LO2}	Γ_{LO2}
300	0.7	8100	220	391	16	0.6	7700	190	482	39
100	0.8	8000	205	389	6	0.5	7950	175	484	22
10	0.5	8400	250	387	2	0.5	8050	200	485	16

out their values at the three temperatures and at both resonances 1 and 2, assuming that spread as the final error on the parameters. We thus obtain at any T, $d = 0.6 \pm 0.2$ nm, $\omega_p = 8050 \pm 400$ cm^{-1}, and $\Gamma_D = 220 \pm 30$ cm^{-1}. By using the Drude formula for the plasma frequency $\omega_p = [(Ne^2)/(\epsilon_0 m^* m_e)]^{1/2}$ (in rad/s), where N is the bulk charge density, $m^* \simeq 0.20$ is the carrier effective mass[28], and m_e the electron mass, one finds $N = (1.3 \pm 0.1) \times 10^{20}$ cm^{-3}. This leads to a surface charge density $n_s = (8 \pm 2) \times 10^{12}$ cm^{-2} and, from the above value of Γ_D, to a carrier mobility $\mu^{IR} = 290 \pm 30$ cm^2/Vs. The former value is in very good agreement with the independent determination of $n_s \sim 1.9 \times 10^{13}$ cm^{-2}, measured in Ref. 28 in the THz range, for the total charge density on both Bi_2Se_3 surfaces. This reduces to $n_s \sim 9 \times 10^{12}$ cm^{-2} for the TI/sapphire interface only, observed here, by assuming in a first approximation that the two charge densities are the same. The present value of the mobility, in turn, can be compared with the previous dc estimates $\mu^{dc} = 400$ cm^2/Vs of Ref. 8, or μ^{dc} from 350 to 1500 cm^2/Vs (depending on the film thickness) of Ref. 29. Also the present determination of the 2DES thickness at the surface of a topological insulator, the first optical one to our knowledge, is close to the value reported in Ref. 8.

The results reported in Table I can greatly help to identify the nature of the 2DES that we have observed here. As already mentioned, three species of free charges may contribute to the surface conductance: a) TSS; b) electrons from impurities and vacancies randomly

distributed close to the surface; c) electrons from impurities and vacancies which accumulate below the surface due to band folding effects. On one hand, the spurious charges of b) and c) type are expected to be few for the following reasons: these MBE-grown Bi_2Se_3 films have been demonstrated in previous experiments[6,8] to be extremely pure, and the present value of $n_s = (8 \pm 2) \times 10^{12}$ cm^{-2} agrees with that extracted from those experiments (9×10^{12}). Moreover, n_s is constant between 10 and 300 K, while it should rapidly increase with T in case of impurity ionization. On the other hand, two important findings are consistent with the attribution of the 2DES to TSS. First, as already mentioned, its thickness $d \sim 1$ nm, smaller by two orders of magnitude than that of the Bi_2Se_3 film, is coherent with dc results[8]. Secondly, the relaxation rate Γ_D is constant with temperature, within errors, as already suggested by plasmonic experiments[11] and expected for the TSS, which are extremely robust against non magnetic scattering processes.

In conclusion, we have used the Berreman effect to investigate, at wavelengths larger by three or four orders of magnitude than the thickness of the system to be investigated, the electrodynamics of the interface between a high-purity thin film of the topological insulator Bi_2Se_3 and its sapphire substrate. Indeed the layer at the interface film/vacuum does not contribute to the present observations, due to the nature of the BE and to its negligible direct absorption. Moreover, any interaction between the two opposite TSS is excluded by the large Bi_2Se_3 film thickness. By accurate fits to the Berreman resonances at the reflectivity edges of two LO phonons of sapphire we have determined for the 2DES a surface density and a mobility consistent with previous determinations on the same system by different techniques. The Fresnel formulas which fit to data the expression for the change in the ellipsometric angle $\Delta\Psi$ induced by the 2DES show that its thickness is smaller than 1 nm. Not only this value obviously excludes that the observed conducting layer is the Bi_2Se_3 film itself, 120 nm thick, but it is also too small for a 2DES formed of charges accumulated by band bending below the interface. Estimates on the order of 1 nm have instead proposed in the literature for the thickness of the TSS layer. Moreover, the extension of the present measurements to low temperature has shown that the Drude parameters of the 2DES are basically independent of T, demonstrating that i) the charges are not thermally activated, as if they were produced from impurities or vacancies; ii) they are extremely robust against scattering processes. Thus, all our findings consistently point toward the conclusion that the 2DES revealed by the Berreman effect is formed by topological surface states, whose

infrared response has been detected here.

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[1] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **95**, 226801 (2005).

[2] M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).

[3] J. E. Moore, Nature **464**, 194 (2010).

[4] H. Zhang, C. -X. Liu, X. -L. Qi, X. Dai, Z. Fang and S. -C. Zhang, Nat. Phys. **5**, 438 (2009).

[5] N. P. Butch, K. Kirshenbaum, P. Syers, A. B. Sushkov, G. S. Jenkins, H. D. Drew, and J. Paglione, Phys.Rev. B **81**, 241301 (2010).

[6] M. Brahlek, N. Koirala, N. Bansal, and S. Oh, Solid State Commun. **215-216**, **54** (2014).

[7] Y. Zhang et al., Nature Phys. **6**, 584 (2010).

[8] N. Bansal, Y. S. Kim, M. Brahlek, E. Edrey, and S. Oh, Phys. Rev. Lett. **109**, 116804 (2012).

[9] M. Basletic, J.-L. Maurice, C. Carrero, G. Herranz, O. Copie, M. Bibes, E. Jacquet, K. Bouzehouane, S. Fusil and A. Barthélémy, Nature Mat. **7**, 621 (2008).

[10] A. Nucara, M. Corasaniti, A. Kalaboukhov, M. Ortolani, E. Falsetti, A. Sambri, F. Miletto Granozio, F. Capitani, J.-B. Brubach, P. Roy, U. Schade, and P. Calvani, Phys. Rev. B **97**, 155126 (2018).

[11] P. Di Pietro, M. Ortolani, O. Limaj, A. Di Gaspare, V. Giliberti, F. Giorgianni, M. Brahlek, N. Bansal, N. Koirala, S. Oh, P. Calvani, S. Lupi, Nat. Nanotechnol. **8**, 556 (2013).

[12] T. P. Ginley and S. Law, Adv. Opt. Mater. 1800113, (2018).

[13] D. W. Berreman, Phys Rev. **130**, 2193 (1963).

[14] A. Dubroka, M. Rössle, K. W. Kim, V. K. Malik, L. Schultz, S. Thiel, C. W. Schneider, J.

Mannhart, G. Herranz, O. Copie, M. Bibes, A. Barthélémy, and C. Bernhard, Phys. Rev. Lett. **104**, 156807 (2010).

[15] M. Yazdi-Rizi, P. Marsik, B.P.P. Mallett, K. Sen, A. Cerreta, A. Dubroka, M. Scigaj, F. Sánchez, G. Herranz and C. Bernhard, Phys. Rev. B **95**, 195107 (2017).

[16] P. Di Pietro, F. M. Vitucci, D. Nicoletti, L. Baldassarre, P. Calvani, R. Cava, Y. S. Hor, U. Schade, and S. Lupi, Phys. Rev. B **86**, 045439 (2012).

[17] B. Harbecke, B. Heinz, and P. Grosse, Appl. Phys. A **38**, 263 (1985).

[18] R. E. V. Profumo, R. Asgari, M. Polini, and A. H. MacDonald, Phys. Rev. B **85**, 085443 (2012).

[19] M. Dressel and G. Grüner, *Electrodynamics of solids*, Cambridge Univ. Press, 2002.

[20] N. Bansal, Y.-S. Kim, El. Edrey, M. Brahlek, Y.Horibe, K. Iida, M. Tanimura, G.-H. Li, T. Feng, H.-D. Lee, T. Gustafsson, E. Andrei, and S. Oh, Thin Solid Films **520**, 224 (2011).

[21] P. Roy, J.-B. Brubach, P. Calvani, G. De Marzi, A. Filabozzi, A. Gerschel, P. Giura, S. Lupi, O. Marcouillé, A. Mermet, A. Nucara, A. Paolone, and M. Vervloet, Nucl. Instrum. & Meth. A, **467-468**, 426 (2001).

[22] P. Roy, M. Rouzires, Z. Qi, O. Chubar, Infrared Phys. & Techn. **49**, 139 (2006).

[23] M. Schubert, T. E. Tiwald, and C. M. Herzinger, Phys. Rev. B **61**, 8187 (2000).

[24] G. Yu, N. L. Rowell, and D. J. Lockwood, J. Vac. Sci. & Tech. A **22**, 1110 (2004).

[25] S. Y. Park and A. J. Millis, Phys. Rev. B **87**, 205145 (2013).

[26] F. Gervais, J.-L. Servoin, A. Baratoff, J. G. Bednorz, and G. Binnig, Phys. Rev. B. **47**, 8187 (1993).

[27] See Supplemental Material at http://xxx for details of data analysis, explanation of the assumptions made, and phonon parameters of sapphire.

[28] L.Wu, W. K.Tse, M. Brahlek, C. M. Morris, R. Valdés Aguilar, N. Koirala, S. Oh, and N. P. Armitage, Phys. Rev. Lett. **115**, 217602 (2015).

[29] K. Dohunl, S. Cho, N. P. Butch, P. Syers, K. Kirshenbaum, S. Adam, J. Paglione and M. S. Fuhrer, Nature Phys. **8**, 459-463 (2012).

[30] Y. Zhang *et al.*, Nat. Phys. **6**, 584 (2010).