Nuclear magnetic resonance (NMR) and transport measurements have been performed at high magnetic fields and low temperatures in a series of n-type Bi$_2$Se$_3$ crystals. In low density samples, a complete spin polarization of the electronic system is achieved, as observed from the saturation of the isotropic component of the $^{209}$Bi NMR shift above a certain magnetic field. The corresponding transport measurements show that the spin degree of freedom can be reliably and directly accessed through such measurements is therefore still pending, and constitute the main motivation of this work.

In this letter, we present a large body of NMR and transport measurements showing that the spin degree of freedom of bulk electronic states in Bi$_2$Se$_3$ can be probed via the hyperfine interaction with the Bi nuclei. This is evidenced by the observation of specific high magnetic fields features in the $^{209}$Bi NMR shift in n-type Bi$_2$Se$_3$ single crystals. In the lowest density samples, the complete spin polarization of the conduction electrons can be achieved, as indicated by the saturation of the isotropic component of the NMR shift above a density-dependent magnetic field. This allows us to precisely estimate the “contact term” of the hyperfine coupling, providing information on the spatial distribution of the electronic wave function, and to determine the amplitude and sign of an effective electronic $g$-factor describing the spin splitting in Bi$_2$Se$_3$. The “contact term” is of the same order of magnitude as in the typical semiconductors with $s$-like electron wave function in the conduction band, in spite of the $p$-type nature of electrons in Bi$_2$Se$_3$ anticipated in the theoretical models near the bulk band gap of this topological insulator. A more complex magnetic field behavior is observed for the anisotropic component of the Knight shift usually related to $p$-like electrons. Our results pave the way for future unconventional experiments such as resistively or optically-detected NMR aiming at testing the spin-physics of the surfaces states in Bi-based topological insulators.

The Bi$_2$Se$_3$ crystals studied in this work were grown...
by the vertical Bridgman method \[15\]. Several batches with different amount of vacancies, known to act as an n-type dopant in Bi$_2$Se$_3$, were prepared to obtain n-type samples with different carrier concentration. A complete characterization of the samples has been obtained by using temperature- and angular-dependent magneto transport experiments \[16\]. Our sample pool cover a Fermi energy range spanning 18-137 meV from the bottom of the conduction band, corresponding to electron densities $n_e$ from $7.5 \times 10^{17}$ cm$^{-3}$ to $1.6 \times 10^{19}$ cm$^{-3}$. NMR measurements were performed both in superconducting magnets (6.5 - 17 T) and in a 20 MW resistive magnet (up to 30 T) \[17\].

**FIG. 1:** (color online) Raw frequency-swept NMR spectra of sample P3-6 ($n_e = 7.5 \times 10^{17}$ cm$^{-3}$) as a function of the magnetic field $B$ parallel to the c-axis at $T = 5$ K. The vertical offset between the spectra is linear in $B$. The open circles denote the fitted NMR line positions, while the connecting dash lines are guide to eye. The frequency axis origin is defined by $f_0 = \gamma B$, the resonance for the bare $^{209}$Bi nuclei ($\gamma = 6.84184$ MHz/T) at the magnetic field calibrated by the $^{27}$Al NMR of an aluminium reference foil placed inside the sample coil.

Figure 1 shows a typical quadrupolar split $^{209}$Bi NMR spectrum at 5 K and its evolution with the magnetic field $B$ parallel to the crystal c-axis. The spectrum consists of a central line and four pairs of satellites due to the quadrupolar coupling between the nuclear spin $I = \frac{5}{2}$ charge distribution and the electric field gradients in the crystal. The main $^{209}$Bi NMR central line is positively shifted compared to the expected position of the bare Bi resonance. In metals and semiconductor, this shift includes the “Knight shift”, due to the interaction between the free carriers and the nuclei, which is our main focus of interest in this paper. As can be seen in figure 1, both the central line and its satellites shift to higher frequencies as the magnetic field increases up to $\sim 15$ T, where they show a sudden drop in frequency. The resonance position then tends to even out in magnetic fields higher than $\sim 22$ T. The field dependence of the frequency shift ($f - f_0$) of the $^{209}$Bi NMR central line observed in figure 1 is plotted in figure 2 for three different samples. The position of the central line was determined by a multiple Lorentzian fit of the entire spectrum with a fixed quadrupolar splitting between the satellites.

**FIG. 2:** (color online) NMR frequency shift ($f - f_0$) of the Bi central line as a function of the magnetic field $B$ applied along the c-axis, for three samples having different carrier concentrations (specified in the figure). $T = 5$ K.

At low magnetic field, the shift increases (approximatively) linearly for all samples. At a fixed magnetic field, it increases with the electron density \[18\]. For samples P3-6 and P2-41 a pronounced kink appears in the NMR shift for magnetic fields of about 15 T and 21 T, respectively. For the high density sample (P1-A1), no saturation is observed in the studied field range. These simple observations of density dependent features in the shift points towards the influence of the conduction electrons. In the simplest approach, the hyperfine contact term gives rise to an effective magnetic field proportional to the total number of free carriers $n_e$ and their spin polarization $P = (n_\uparrow - n_\downarrow)/n_e$, where $n_\uparrow$ and $n_\downarrow$ are the number of spin up and down in the system, respectively. This leads to an NMR frequency shift which is directly connected to the spin polarization of the system. In a bulk semiconductor the spin polarization is primarily determined by the ratio between the Zeeman and Fermi energies and increases with the magnetic field. In sufficiently high magnetic fields (or low Fermi energies), a complete spin polarization of the system can in princi-
ple be achieved, leading to a saturation of the internal effective magnetic field seen by the nucleus, and thus a saturation of the NMR frequency shift. This joint condition of a low Fermi energy and a high Zeeman energy can however only be experimentally realized in dilute 3D electronic systems under relatively high magnetic fields. To our knowledge, a saturation of the NMR Knight shift has only been observed in InSb so far [19][21], where the effective electron g-factor is about -51.

In Bi$_2$Se$_3$, the bulk magneto-transport properties have been successfully described in the pioneering work of Köhler [22], using a model of a 3D electron gas with an energy-dependent anisotropic Fermi surface and a spin splitting described by an effective g-factor $g_{eff}^s = 32\pm 3$. This approach was confirmed more recently in thermal transport measurements [23], and can also be used to describe the results of our magneto-transport measurements [24]. A saturation of the Knight shift is then predicted for a magnetic field $B_s$ which is defined by $g_{eff}^s \mu_B B_s = 2\pi E_F$, where $E_F$ is the zero-field Fermi energy [25]. For samples P3-6 and P2-41, our transport experiments yield $E_F = 19.7$ and 26.4 meV respectively, which with $g_{eff}^s = 32.5$ gives corresponding values of $B_s = 16.6$ and 22.2 T, close to the observed kinks in figure 2. The absence of any deviation of the shift in the higher carrier concentration sample is also expected since the much higher Fermi energy pushes $B_s$ far outside of our observable range. These very simple arguments points toward a direct connection between the electronic spin polarization and the NMR Knight shift in Bi$_2$Se$_3$.

We note, however, that for sample P3-6 a clear saturation of the Knight shift to a maximum value is not observed: the shift rather slowly drops down and appears to saturate to a lower value above 22 T. This behavior has been confirmed for different samples of similar density and is also to some extent present for sample P2-41. For a deeper understanding of our data, one should consider the general expression of the hyperfine coupling Hamiltonian in metals or doped-semiconductors [25]:

$$\mathcal{H}_{HF} = \frac{\mu_0}{4\pi} g_0 \mu_B \gamma \hbar \left[ \frac{8\pi}{3} S \delta(r) - \frac{S}{r^3} - \frac{3(S \cdot r) r}{r^5} + \frac{1}{r^3} \right],$$

where $g_0$ and $\mu_B$ are the electronic bare g-factor and Bohr magneton, respectively, $\gamma$ is the nuclear gyromagnetic ratio, $I$ and $S$ are the nuclear and electronic spin respectively, $r$ is the electron-nuclei position vector and $I$ the orbital momentum of the conduction electron. The first term in the bracket is the “contact” hyperfine interaction, which originates from the density probability of the electron exactly at the nuclear site ($r = 0$). This coupling is de facto isotropic and dominates the hyperfine interaction in the case of an $s$-like electronic wave function. This yields a direct access to the electronic spin polarization (see a recent example in a GaAs 2D electron gas [13][14]). The second term is anisotropic and results from the dipolar coupling between nuclear and electronic moment away from the $r = 0$ singularity, which dominates in the case of $p$-like electronic wave function (see e.g. Ref. 9[27]. The last term is related to the orbital momentum of the conduction electrons. As usual in solids with non-degenerate orbital levels, which is the case for Bi$_2$Se$_3$ [1][12], the average orbital momentum $< 1 \theta > = 0$, and this term only gives rise to a second order contribution [28].

The main contributions will thus a priori come from the first two terms, whose relative weights mainly depend on the nature of the electronic wave function. Very recently, the presence of both anisotropic and isotropic contributions in the total NMR shift in Bi$_2$Se$_3$ has been reported at low carrier density [10]. To further investigate the origin of the observed downturn in high magnetic fields (Fig 2), we have performed angular dependent measurements of the NMR shift in our lowest density sample. For the axial symmetry, present in Bi$_2$Se$_3$, one can decompose the total frequency shift $\Delta f$ into two contributions, an isotropic contribution $\Delta f_{iso}$ and an anisotropic one $\Delta f_{axial}$, by writing $\Delta f = \Delta f_{iso} + \Delta f_{axial}$. As argued above, only the dipolar term contributes to $\Delta f_{axial}$ and the total shift can be written with an explicit angular dependence as $\Delta f = [A_{iso} + (3\cos^2\theta - 1)A_{axial}]n_e \times P(\theta)$ where $\theta$ is the angle between the magnetic field $B$ and the c-axis. $A_{iso}$ and $A_{axial}$ are the “contact” and “dipolar” hyperfine coupling constants, respectively, and the spin polarization $P$ may depend on $\theta$ in the case of anisotropic conduction band parameters. The isotropic and the axial part of the shift can be extracted from the rotational pattern of the central line [29]. Figure 3 shows the isotropic and axial components of the frequency shift for sample P3-6.

A clear saturation of the isotropic components of the Knight shift is observed above 16 T, and can be attributed, as discussed above, to the full spin polarization of the electronic system manifesting itself directly through the “contact” term of the hyperfine coupling. The frequency shift can be calculated by writing $\Delta f_{iso} = A_{iso} \times n_e \times P$, where the spin polarization $P$ is calculated in the simple 3D electron gas model introduced above. The two free parameters of this model, $g_{eff}^s$ and $A_{iso}$, can be determined independently. As the Fermi energy is precisely estimated from transport measurements, $g_{eff}^s$ is only determined by the position of the saturating field $B_s$. $A_{iso}$ is then adjusted to reproduce the frequency shift value, from the low field region to the saturation. The result of this simulation is plotted as a dotted line in figure 3 and catches the observed saturation very well [30].

An even better agreement with the experimental data can further be obtained by incorporating additional elements to our model, such as the Landau quantization of the electronic density of states (fully characterized from transport experiments [16]) and the effect of disorder which reduces the spin polarization through a
level broadening. The result is plotted as solid line in figure 3 and gives a perfect quantitative description of our experimental data. Small modulations of the Knight shift can even be observed and attributed to the effect of the Landau quantization on the spin polarization, see e.g. the shallow downturn around 10.8 T. In the case of Bi₂Se₃ the characteristics of these oscillations reflects, in particular, the peculiar commensurability of the spin and cyclotron gap [24]. The obtained effective electron g-factor is $g_{e ff}^e = +32.8 \pm 1$, in a very good agreement with transport experiments performed on the same samples [24], and the previously reported value of 32±3 [22]. We note that, in contrast to transport experiments, NMR experiments unambiguously determines the sign of the g-factor which directly impacts the sign of the Knight shift. The extracted value of the “contact” hyperfine coupling constant $A_{iso} = 6.94 \pm 0.16 \times 10^{-13} cm^3/s$ enables us to estimate the density of the electronic wave function at the nuclear site $d_{Bi} = 8.72 \times 10^{25} cm^{-3}$ [31].

The obtained values of $A_{iso}$ and $d_{Bi}$ are comparable to or even higher than values determined for GaAs electron systems exhibiting pure s-like wave function (e.g. $A_{iso} = 4.5 \pm 0.2 \times 10^{-13} cm^3/s$ [32] and $d_{Ga} = 5.8 \times 10^{25} cm^{-3}$ [33] for $^{71}$Ga in GaAs). This is at first sight surprising, since from a low energy expansion around the Dirac point [1], it is expected that the wave function describing the Dirac surface states, as well as the one describing the bulk conduction band minimum (CBM) and bulk valence band maximum (VBM) states, is of p-wave nature. This originates from the combination of p-orbitals of Bi and Se atoms [1] [12]. In this case, the NMR shift produced by conduction electrons should be, at least at low energy, purely anisotropic. Our results, showing a very large isotropic component in the Knight shift for Fermi energies as low as 18 meV, therefore cannot be understood within this approach. They suggest that a significant portions of the electronic wavefunction is of s-wave nature. In fact, our results could be consistent with very recent theoretical results [34] showing that about 10 % of the electronic wave function at the Bi sites are of s-wave nature, emerging from deeper Bi “6s” orbitals taking part in shaping the wave function both in the VBM and CBM. This could explain the origin of the large isotropic component evidenced in the Bi NMR. Another interesting results of these calculations is the apparent absence of a s-like wave function at the Se site: this is consistent with the smaller shift observed at the same magnetic field for the $^{77}$Se NMR [35] and the extremely large relaxation time, showing a weaker coupling of the Se nuclei to the conduction electrons. The remaining dominant p-wave nature of these wave functions leads to the anisotropic dipolar term in the $^{209}$Bi NMR shift. The negative sign of this term (Fig.3), consistent with recent results [10], suggests that a significant fraction of the p orbitals (more than $\frac{1}{3}$) is of $p_x$ rather theoretically expected $p_z$ nature [1]. Recent results of Ref. [34] reveal the presence of a non-negligible $p_{xy}$ component (20 % at the CBM and 40 % at the VBM) which could be at the origin of our observation, even though this percentage is still too small to account for a sign change in the dipolar term. The magnetic field behavior of the anisotropic shift turns out to be more complex than the one of the isotropic component, as can be seen in figure 3 [36]. This illustrates the importance of having a sizeable isotropic component in the Knight shift as a reliable and direct access to the electronic spin polarization.

We finally note that the temperature dependence of the Knight shift measured on our samples [37], constitutes an additional manifestation of the direct connection between the NMR shift and the electronic spin polarization and confirms our general approach.

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[13] The transport experiments performed on our samples are present in the supplemental material, section I. The main physical parameters, i.e. effective mass, Fermi energy, Fermi surface anisotropy and carrier concentration are listed in Table 1 therein.

[14] See supplemental material, section III.A for more experimental details.

[15] The density dependence of the total shift is analyzed in detail in the supplemental material, section III.D.

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