It is now generally accepted that MgB$_2$ is a phonon mediated superconductor\cite{simon1, simon2, simon3} which owes its unusual properties to the widely different electron-phonon couplings on its disconnected Fermi surface (FS) sheets\cite{simon4}. The two-gap model assumes a large superconductor gap for the cylindrical sheets originating from B-B $\sigma$ bonds and a smaller gap for the FS sheet of $\pi$ electrons. It describes physical properties such as the temperature dependent specific heat\cite{simon5} and tunneling\cite{simon6} successfully in zero magnetic field, predictions in finite fields are much less tested. Recent experiments show that magnetic fields as low as $H_{c2}^\alpha \approx$1 T close the smaller, $\pi$-gap\cite{simon7, simon8, simon9, simon10}. The stronger electron-phonon coupling for $\sigma$ electron states maintains the superconductivity above 1 T. Yet, there has been no microscopic description of this phenomenon. The cylinder-like FS sheets of the $\sigma$ bands are responsible for the anisotropy of the upper critical field, $H_{c2}^\alpha = 16$ T and $H_{c2}^\pi$ about 2.5 T\cite{simon11, simon12, simon13}. Band calculations\cite{simon14} estimate that about half of the density of states (DOS) is on the $\pi$ band thus the two-gap model predicts that closing the gap at 1 T restores about half of the normal state DOS. Naively, one would expect that properties proportional to the DOS, like the specific heat coefficient or the spin-susceptibility should reach half of their normal state values at about 1 T, whereas the remaining half originating from the $\sigma$ bands should be restored gradually with further increasing the field to $H_{c2}$.

In this Letter, we report on the magnetic field dependence of the conduction electron spin-susceptibility, $\chi_s$, in the superconducting state of high purity MgB$_2$ powders. This is the first time $\chi_s$ is measured using conduction electron spin resonance below $T_c$ in a superconductor. We observe an unusually strong increase of $\chi_s$ with the magnetic field, $H$, which cannot be reconciled with current models easily. The DOS induced by fields well below $H_{c2}$ is larger than 50 $\%$, the value expected from closing the gap on the $\pi$ band FS only.

We studied samples from several batches. Sample 1 is made from 99.99 $\%$ purity natural isotopic mixture of $^{10}$B and $^{11}$B amorphous boron, Samples 2 and 3 are made from crystalline, isotopically pure $^{11}$B. Chemical analysis, the high normal state conductivities and narrow CESR lines at $T_c$ attest the high purity of the samples. Details of sample characterization are discussed in Ref.\cite{simon15}. Sample 2 was made from the batch used in the CESR work of Ref.\cite{simon16}. Fine powders with grain sizes less than 1 $\mu$m were selected from the starting materials to reduce the inhomogeneity of microwave excitation. The aggregates of small grains of the starting materials were first thoroughly hand-crushed in a boron carbide mortar. The resulting powders were suspended in isopropanol and mixed in a 1:1 weight ratio with pure SnO$_2$ fine powder. The larger particles were eliminated by sedimentation for long times or in a centrifuge and the small grains were extracted from the suspension by filtering. Mixing with SnO$_2$ is important to separate the MgB$_2$ particles to avoid eddy-currents. SEM microscopy has confirmed that this procedure results in MgB$_2$ grains smaller than 0.5 $\mu$m size. SQUID magnetometry of the original batch and the final fine powders confirmed that superconducting properties were not affected by this procedure. The powders were finally cast into epoxy for the ESR experiments. We detail CESR experiments at 3.8, 9.4 and 35 GHz at fields near 0.14, 0.34 and 1.28 T respectively. The CESR results at higher frequencies of Ref.\cite{simon16} were also reproduced and we confirmed that the minimum value of the higher upper critical field, $H_{c2}^{\text{min}}$, is somewhat below 2.7 T. $\chi_s$ of MgB$_2$ was measured from the intensity of the CESR with no need for core electron corrections. Fine powder of the air stable metallic polymer, o-KC$_6$0 was mixed into the epoxy for some of the samples to serve as a temperature independent ESR in-
The room temperature peak-to-peak linewidth, $\Delta H_{pp}$ = 111 ± 3 G, of the derivative absorption line is dominated by spin-lattice relaxation due to phonons. The residual linewidth at 40 K arises from static imperfections and is sample dependent. The residual linewidth is somewhat smaller for Sample 1 ($\Delta H_{pp}$ = 10 ± 0.3 G), than for Sample 2 (2.3), (11 ± 0.3 and 20 ± 0.6 G) while the residual resistance ratio (RRR) is larger for the latter two samples [14]. Unlike the RRR, the CESR linewidth is insensitive to intergrain scattering and the difference may be related to the different morphology of Sample 1 and (2,3). The small asymmetry of the lineshape ($A/B=1.16$ for Sample 1) at 40 K shows that microwave penetration is nearly homogeneous [14], the nominal particle size is in the range of the microwave penetration depth, $\delta=0.3 \mu m$, and the reduction of the CESR signal intensity due to screening is less than 5 %.

Above 450 K (data not shown), the CESR intensities are the same for the three samples and correspond to a susceptibility of $\chi_s$ = (2.3 ± 0.3) x 10^{-5} emu/mol in agreement with the previously measured value [11] of $\chi_s$ = (2.0 ± 0.3) x 10^{-5} emu/mol and calculations of the DOS [3]. In Sample 1, the CESR intensity is nearly $T$ independent in the normal state, the measured small decrease of about 20 % between 600 and 40 K is of the order of experimental precision at high temperatures. In Sample 2 and 3 the CESR intensity decreased by a factor of 2.5 between 450 and 40 K. The nearly symmetric Lorentzian lineshape showed that this intensity decrease is not due to a limited penetration depth. Neither does the intensity decrease correspond to a change in $\chi_s$. We measured the $T$ dependence of the $^{11}$B spin-lattice relaxation time, $T_1$, in Samples 2 and 3 and found a metallic, $T$ independent value of $1/(TT_1)=167\pm 3$ s^{-1} in agreement with Ref. [17] and [18]. It is possible that the difference in morphology and purity at the grain surfaces explains that the CESR signal intensity is almost constant in Sample 1 while it changes strongly in Sample 2 and 3. We believe that the nearly constant CESR intensity and the constant $1/(TT_1)$ measures correctly the metallic susceptibility of MgB2.

Below $T_c$, the $T$ and $H$ dependence of the diamagnetic shifts, linewidths, and intensities normalized at $T_0$ are similar in all three samples. We discuss Sample 1, for which the CESR signal intensity is constant in the normal state within experimental precision. For the applied magnetic fields, $H < H_{c2}^{\text{min}}(T=0 \text{ K})$ and at $T < T_c$ the CESR signal corresponds to the mixed state of the MgB2 superconductor; any non-superconducting fraction would be easily detected as in Ref. [11] for $H > H_{c2}^{\text{min}}$. The ESR of a tiny impurity phase is well outside the CESR of MgB2 (marked by * in Fig. 1). Comparison of the diamagnetic magnetization, $M$, measured by SQUID and the diamagnetic shift of the CESR, $\Delta H_0(T) = H_0(T) - H_0(40 \text{ K})$ ($H_0$ is the resonance field), also verifies

**FIG. 1:** Temperature dependence of the CESR signal of MgB2 fine powder sample (Sample 1) at 9.4 GHz (0.34 T). * denotes the ESR signal of a tiny amount of paramagnetic impurity phase.
that below $T_c$ we detect the CESR of the MgB$_2$ superconductor. Figure 2 shows $\Delta H_0(T)$ at 3 different ESR frequencies and $M$ at the corresponding static magnetic fields with a scaling between $\Delta H_0$ and $M$ as in Ref. [11]. The present diamagnetic shift data on fine grain samples at 35 GHz and higher frequencies (not shown) agrees with our previous report on large grain samples.[11] $\Delta H_0(T)$ is equal to the average decrease of the applied magnetic field in the sample and is proportional within a shape dependent constant to $M$ of the grains. $\Delta H_0(T)$ averaged for increasing and decreasing field sweeps is proportional to $M$ in the field cooled sample with the same proportionality constant in a broad range of $T$’s for all the three magnetic fields. We used the same argument previously to identify the signal of superconducting MgB$_2$ particles in higher frequency (35 GHz) CESR experiment [11].

The CESR line broadens inhomogeneously below $T_c$ due to the macroscopic inhomogeneities of diamagnetic stray fields (data not shown). Within each isolated grain, spin diffusion motionally averages all magnetic field inhomogeneities arising from screening currents or vortices[15] and the modulation of field between vortex cores does not broaden the CESR. The line is however broadened in the randomly oriented powder by the crystalline and shape anisotropy of the diamagnetic shift, that changes from grain to grain. As expected for this case, the observed additional linewidth in the superconducting state, $\Delta H_s$, is proportional to the shift and $\Delta H_s/\Delta H_0(T)$ is about 0.3 at all fields and temperatures.

The main topic of the current report is the measurement of $\chi_s$ in the superconducting state of MgB$_2$. Usually, $\chi_s$ is determined from the measurements of temperature dependent Knight’s shift or spin-lattice relaxation time, $T_1$.[21] To our knowledge, in MgB$_2$ there has been no successful determination of these quantities below $T_c$; precision of the Knight shift measurement is limited due to the diamagnetic magnetization[17][21], while $T_1$ measurements are affected by several factors like vortex motion[17]. In CESR, the signal intensity is proportional to $\chi_s$ and diamagnetism affects only the shift of the resonance line. $\chi_s$ is proportional to the DOS of normal excitations when electron correlations are small.

In Figure 3, we show $\chi_s$ below 60 K measured at three magnetic fields. The 9.4 GHz (0.34 T) and 35 GHz (1.28 T) data are normalized at 40 K while the 3.8 GHz (0.14 T) data are normalized at 100 K. At 3.8 GHz and 35 GHz data are missing in ranges of 36 to 100 K and 27 to 34 K, respectively, where the CESR of MgB$_2$ could not be resolved from the KC$_{60}$ reference. Data taken at 9.4 GHz with and without reference agree well and the data without reference are shown. Irreversibility does not affect the measurement of $\chi_s$ in the studied range of $T$ and $H$: linewidths and shifts depend on the direction of the field sweep at low $T$ but the intensities are the same within 5% that is our experimental precision at low $T$. In Fig. 3, data at 9.4 and 35 GHz are averaged for sweeps with increasing and decreasing fields while at 3.8 GHz decreasing field sweep data are shown. No correction is made for diamagnetic screening of the microwave excitation, this would increase somewhat further the measured values of $\chi_s$.

The $T$ dependent $\chi_s$ at our lowest magnetic field, 0.14 T, lies well above $\chi_s(T, H = 0)$ (dashed curve in Fig. 3) calculated for an isotropic $T_c = 39$ K weak coupling BCS superconductor[22]. The measured $\chi_s$ at 0.14 T is compatible with the two gap model above 10 K. The solid curve in Fig. 3 shows $\chi_s(T, H = 0)$ calculated within the model of two independent gaps. We used $\Delta_1(T = 0) = 11$ K and $\Delta_2(T=0)=45$ K, with DOS equally shared on the two Fermi surfaces, and both gaps opening at $T_c$. The choice of these parameters is in agreement with experimental results[5][6][23] and theoretical estimates[4].

The remarkably large field induced $\chi_s$ observed at 0.34 and 1.28 T at all $T$’s below $T_c$ is the main finding of this work. These fields are much smaller than the upper critical fields, $H_{c2} \sim 2.5$ T[11][12][13] and $H_{c2}^{ab} \sim 16$ T. Unlike in usual superconductors, $\chi_s$ at $T_c/2$ is still near to its normal state value and remains large at the lowest $T$’s: $\chi_s(4 \text{ K})/\chi_s(40 \text{ K}) = 0.46 \pm 0.06$ at 0.34 T and $\chi_s(3 \text{ K})/\chi_s(40 \text{ K}) = 0.87 \pm 0.06$ at 1.28 T. As shown in Fig. 4, the measured $\chi_s$ at low $T$ is in rough agreement with the specific heat measured on a powder sample (solid curve in Fig. 4) but we find an even stronger field dependence. The specific heat data, unlike the $\chi_s$ data, are affected by the electron-phonon enhancement which varies strongly between the different FS sheets. The data cannot be described by a simple anisotropic superconductor. The dashed curve in Fig. 3 shows the calculated field dependence of $\chi_s$ of a powder of an anisotropic superconductor with $H_{c2} \sim 2$ T and $H_{c2}^{ab} \sim 16$ T at $T=0$. Here,
we assumed a Landau-Ginzburg type angular dependence of \( H_{c2}(\theta) \) as described in Ref. 11 and a contribution to \( \chi_s \) proportional to \( H/H_{c2}(\theta) \) for each superconducting grain. As seen in Fig. 4, this description is inadequate. A better approximation is obtained if, following Ref. 7, one assumes that the \( \pi \) band FS is restored at around \( H \sim 1 \) T and the observed anisotropic \( H_{c2} \) arises solely from the \( \sigma \) band. In Fig. 4 we show this case with dotted lines, assuming that 50% of the DOS is already restored at \( H = 0.5 \) T. However, this simple minded application of the two-gap model is still inadequate: the large value of \( \chi_s \) at 1.28 T and 3 K, and the \( T \) dependence at 0.34 T, in particular the restoration of the full DOS at 25 K, remain unexplained.

In conclusion, the magnetic field dependence of the spin-susceptibility in MgB\(_2\) shows that a large part of the Fermi surface is restored at fields well below the minimum of the upper critical field. These observations pose a challenge to theory since they cannot be explained with an anisotropic superconductor model nor by simple application of the two-gap model even if it is assumed that the \( \pi \) band FS is restored at magnetic fields as low as \( 0.1 H_{c2}^{\min} \).

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