Anisotropy of superconducting MgB$_2$ as seen in electron spin resonance and magnetization data

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We have observed the conduction electron spin resonance (CESR) in fine powders of MgB$_2$ both in the superconducting and normal states. The Pauli susceptibility is $\chi_s=2.0\cdot10^{-5}$ emu/mole in the temperature range of 450 to 600 K. The spin relaxation rate has an anomalous temperature dependence. The CESR measured below $T_c$ at several frequencies suggests that MgB$_2$ is a strongly anisotropic superconductor with the upper critical field, $H_{c2}$, ranging between 2 and 16 T. The high-field reversible magnetization data of a randomly oriented powder sample are well described assuming that MgB$_2$ is an anisotropic superconductor with $H_{c2}^b/H_{c2}^c \approx 6-9$.

74.70.Ad, 74.25.Nf, 76.30.Pk, 74.25.Ha

Following the recent discovery of superconductivity in MgB$_2$ several of its fundamental properties have been established. MgB$_2$ is a type II superconductor with $\lambda \approx 140$ nm and the upper critical field $H_{c2} \approx 16$ T. The question to what degree this superconductor is anisotropic is still unresolved, the reason being the lack of single crystals of size sufficient for direct measurements. The anisotropy is an important characteristic both for the basic understanding of this material and for applications; enough to mention that the anisotropy strongly affects the pinning and critical currents.

An anisotropic or multi-component superconducting gap was inferred from a number of indirect measurements and was suggested in several theoretical descriptions of MgB$_2$. For partially oriented crystallites, the anisotropy ratio is reported as $\gamma = H_{c2}^a/H_{c2}^c = 1.73$, for c-axis oriented films $\gamma \approx 2$, was found. In this Letter, we report estimates of the anisotropy parameter $\gamma$ as high as 6–9, based on two independent techniques which utilize properties of random powders.

Conduction Electron Spin Resonance (CESR) is commonly used to determine the spin susceptibility, $\chi_s$, and the spin relaxation rate, $T_1^{-1}$, in normal metals. The mechanisms inducing conduction electron spin-lattice relaxation are similar to those of momentum relaxation: they are both related to phonons at high temperatures and to the impurity scattering at low- $T$. In the mixed state of superconductors, CESR is observable due to the normal electron states localized in vortex cores and due to quasiparticle excitations over the gap (at finite temperatures). Surprisingly, in powders of MgB$_2$ we also observe the normal phase CESR signal at low $T$'s and in fields well below the reported upper critical field of 16 T. The data suggest that $H_{c2}$ of MgB$_2$ may be strongly anisotropic.

We have used isotopically pure Mg$^{11}$B$_2$ ($T_c=39.2$ K) samples from the same batch as reported elsewhere. The original sample consisted of 100 $\mu$m large aggregates of small grains. The samples were thoroughly ground in a mortar to crush the aggregates. Most of the resulting grains were between 0.5 and 5 $\mu$m in size and were separated by mixing into ESR silent high vacuum grease or SnO$_2$. Crushing the aggregates increased the CESR signal intensity limited by small microwave penetration but did not affect the superconducting properties of the samples: dc magnetization measurements confirmed that $T_c(H)$, the transition width and shielding fraction remained unchanged.

ESR experiments were performed at 9, 35, 75, 150 and 225 GHz at the corresponding resonance magnetic fields of 0.33, 1.28, 2.7, 5.4 and 8.1 T. The spin susceptibility was measured by calibrating the 9 GHz spectrometer (Bruker ESP 300) against CuSO$_4$·5H$_2$O. The 9 GHz spectrometer uses a microwave resonant cavity and the so-called vortex noise generated by the magnetic field modulation prohibits ESR measurements in the superconducting state below the irreversibility line. The High Field ESR spectrometer (Budapest HF-ESR lab, 35 GHz and higher frequencies) does not utilize a resonant cavity thus avoids vortex-noise. The $g$-factor...
was measured with respect to diphenyl-picryl-hydrazyl \((g=2.0036)\) and Mn/MgO \((g=2.0009)\).

The CESR at 9 GHz and above 500 K has the antisymmetric Lorentzian absorption derivative lineshape characteristic of a relaxationally broadened ESR and homogeneous excitation (Fig. 3 inset). We find \(g=2.0019\pm0.0001\) for the \(g\)-factor at 40 K at both 35 GHz and 9 GHz. At 300 K and 9 GHz we get \(g=2.001\pm0.001\). The CESR intensity is temperature independent between 450 and 600 K and the paramagnetic spin susceptibility is \(\chi_p=(2.0\pm0.3)\times10^{-5}\) emu/mole. Assuming negligible electron-electron correlations, the density of states (DOS) at the Fermi level is 0.6 states/eV in agreement with band structure calculations [19]. At lower temperatures, the size of larger grains \((s=5\,\mu m)\) becomes comparable or larger than the skin depth, \(\delta=(\rho/\pi\mu_f)^{1/2}\), and the observed CESR intensity gradually decreases. Here \(\rho\) denotes the specific resistivity of MgB\(_2\), \(\mu_f\) is the vacuum permeability, and \(f\) is the ESR frequency. At 40 K, the ESR intensity is \(\sim25\%\) of the high temperature value in agreement with the decrease in \(\delta\) estimated from the resistance (Fig. 3). At 300 K and 40 K the calculated skin depths at \(f=9\) GHz are \(\delta=1.6\,\mu m\) and \(0.3\,\mu m\), respectively, using values of \(\rho\) measured on dense MgB\(_2\) wires [10].

Below 400 K, deviations from the antisymmetric lineshape appear. In most cases, a \(T\) dependent mixture of Lorentzian derivative absorption and dispersion components simulates well the observed line. Figure 3 shows the \(T\) dependence of the CESR linewidth in the normal state. The Lorentzian lineshape is a signature of a homogeneous line broadening; in this case the half width at half maximum of the Lorentzian absorption line is \(w=1/\gamma_eT_1\), where \(T_1\) is the spin-lattice relaxation time, and \(\gamma_e\) is the electronic gyromagnetic factor. The electron mean free path, \(\ell\), is about 0.06 \(\mu m\) at 40 K [17], thus \(\ell\ll\delta\) and the normal skin effect determines the excitation. At 40 K, the spin mean free path [18], \(\delta_{eff}=1/3\nu_F(T_1\tau)^{1/2}\approx4\,\mu m\) is comparable to the maximum grain size, 5 \(\mu m\), and the conduction electron magnetization is homogeneous. There is a field dependent residual linewidth at low \(T\), followed by a strong increase with temperature and a broad maximum at 450 K. At 40 K and 9 GHz the linewidth is narrow, 15 G. At 40 K and 225 GHz the line is inhomogeneous; it is broadened to about 35 G. The \(T\) dependent contribution to linewidth is independent of the magnetic field.

As expected for a light metal [13], MgB\(_2\) has a \(g\)-factor of 2.0019 close to the free electron value of 2.0023 and a temperature dependent linewidth (proportional to \(1/T_1\)) which follows the resistance below 200 K. However, the maximum in \(1/T_1\) observed in MgB\(_2\) at 450 K has no analogue among pure metals.

Below \(T_c\) the CESR changes dramatically, see Fig. 2. At 35 GHz (1.28 T) there is a single line at all temperatures, and a large \(T\) dependent diamagnetic shift in the field position of the resonance is observed, Fig. 2a-d. The line also broadens, but the broadening is roughly three times less than the shift. Below the irreversibility line \((T_{irr}=31\,K\) at 1.28 T) the penetration of magnetic flux is hysteretic and the line position and width are dependent on the direction of magnetic field sweep. At higher frequencies, above 2.7 T, the CESR line splits in two components, which are well resolved at 5 K. One of these components is situated at the position of the normal state CESR. This suggests that a part of the grains is in the normal state. In other words, there is a distribution of \(H_{c2}\)’s among the grains and in a part of the sample \(H_{c2}\) is as low as about 2 T.

Figure 2 shows the \(T\) dependence of the CESR shift, \(\Delta H_0(T)=H_0(T)-H_0(40\,K)\), at 35 GHz, where \(H_0(T)\) is the resonance field of the ESR spectra. It follows closely the field cooled magnetization \(M(T)\) measured at 1.28 T by SQUID magnetometer shown for comparison. The rough agreement of \(\Delta H_0(T)\) and \(4\pi|M(T)|\) and their similar temperature dependences strongly support that we observe the CESR in the superconducting state. Yet, the CESR line shift below \(T_c\) is not simply proportional to the macroscopic magnetization. Theory and experiment on CESR in superconductors is limited to a few reports (See Ref. [2] and references therein) only.

The complex lineshape seen in Fig. 2ef at higher fields is due to an inhomogeneous distribution of \(\Delta H_0\) among the sample grains. The splitting of the spectra cannot be explained with the variation of the field between vortex cores. Unlike the NMR spectrum, the CESR is not broadened by these short-scale magnetic field variations. Electrons diffuse to large distances within \(T_1\) and a single resonance appears at a well defined average field weighted by the local density of states [21]. In K\(_3\)C\(_{60}\), a fullerene compound with \(T_c=19\,K\) studied in detail [20], the CESR is relatively narrow in the superconducting state and only below \(T_{irr}\) do large scale (typically 1 \(\mu m\)) inhomogeneities of diamagnetism broaden the spectrum.

A substantial part of the spectrum at 2.7 T is not shifted with respect to the normal state and comes from normal state fractions of the sample. In other words, \(H_{c2}\) of the grains within this fraction is smaller than the applied field \(H\), in this case 2.7 T. The upshifted line can be identified as signal coming from superconducting parts of the sample by the similarity of its characteristics to the observed single line at 1.28 T (Fig. 3a); i.e. \(T\) dependent diamagnetic CESR shift and broadening below \(T_c\). The value of \(\Delta H_0\) decreases with increasing field, following the decrease of the superconducting magnetization and its values at \(T=2.5\,K\) are \(\Delta H_0(2.7\,T)=25\,G\), \(\Delta H_0(5.4\,T)=9\,G\), and \(\Delta H_0(8.1\,T)=5\,G\). Thus, the upshifted line (Fig. 3) arises from particles with large \(H_{c2}\). The diamagnetic shift is larger for particles with larger \(H_{c2}\) but since this has a maximum (at 16 T), the derivative CESR spectrum has a relatively narrow peak at the high field end. This peak is marked by an arrow in Fig. 2.
the applied field is increased, the CESR intensity of the superconducting fraction with respect to the intensity of the normal state fraction decreases, Fig. 2 e,f. However, a quantitative determination of the variation of the superconducting fraction is not possible from the CESR lineshape since the variations of the microwave penetration depth and the spin susceptibility with magnetic field and temperature are not known. Nevertheless, our observations provide clear evidence for a low value (≈ 2 T) of minimal $H_{c2}$ in the MgB$_2$ powder. Since the maximum measured $H_{c2}$ is about 16 T [3], we conclude that the sample grains have $H_{c2}$'s spanning from approximately 2 to 16 T.

The anisotropy of MgB$_2$ is a probable cause for the distribution of $H_{c2}$'s in powder samples. It is unlikely that the distribution is due to a spread in the quality of our sample, since the superconducting transition is reproducibly sharp in transport and thermodynamic measurements and the residual resistance ratio of polycrystalline samples, $RRR > 20$, is relatively high [2]. Still, an unexpectedly large anisotropy calls for an independent verification. We did this by analysing the data on the magnetization, $M(H,T)$, of powder samples.

We consider a sample of randomly oriented grains of a uniaxial superconductor with the anisotropy $\gamma = H^{ab}_{c2}/H^{c}_{c2}$ placed in a field $H$ along $z$. The distribution of grains over their $c$ direction is given by $dN = N \sin \theta \, d\theta/2$ with $\theta$ being the angle between $c$ and $H$. The grain upper critical field depends on $\theta$ according to $H_{c2}(\theta) = H^{ab}_{c2}/\sqrt{\epsilon(\theta)}$ with $\epsilon = 1 + (\gamma^2 - 1) \cos^2 \theta$.

In agreement with what is currently known [12], we assume $H^{ab}_{c2} > H^{c}_{c2}$ ($\gamma > 1$) and consider the field domain $H^{c}_{c2} < H < H^{ab}_{c2}$ following the procedure of [23]. Clearly, only the grains with $H_{c2}(\theta) > H$ contribute to the superconducting magnetization. The grain orientation $\theta_0$, for which the given $H$ is the upper critical field is given by $\cos^2 \theta_0 = [(H^{ab}_{c2}/H)^2 - 1]/(\gamma^2 - 1)$. We then have for the magnetization $M_z = \int_{\theta_0}^{\pi/2} M_z(\theta, H) \sin \theta \, d\theta$, while the transverse component of $\mathbf{M}$ averages to zero. According to Ref. [23], the magnetization of the grain near its $H_{c2}$ is given by

$$-4\pi M_z = \frac{H_{c2}(\theta) - H}{2\kappa^2 \beta \gamma^{3/2}} \epsilon(\theta),$$

(1)

Here, $\beta = 1.16$ and we assumed the Ginzburg-Landau parameter $\kappa \gg 1$. We then obtain after simple algebra:

$$M_z = -M_0 \, f(h), \quad M_0 = \frac{\phi_0}{2\pi^2 \lambda^2 \beta \gamma^{1/3} \sqrt{\gamma^2 - 1}},$$

(2)

$$f(h) = \frac{1 - 4h^2}{3h^2} \sqrt{1 - h^2} + \ln \frac{1 + \sqrt{1 - h^2}}{h},$$

(3)

where $h = H/H^{ab}_{c2}$ and $\lambda = (\lambda^{ab}_{c2} \lambda_{c2})^{1/3}$ is the average penetration depth. It is seen that as $H \to H^{ab}_{c2}$, $M_z \propto (H^{ab}_{c2} - H)^{3/2}$, i.e. in a polycrystal $M(H)$ decreases faster than for a single crystal.

Figure 4 shows the reversible part of $M(H)$ for a few temperatures, along with solid curves obtained by fitting the data to Eqs. (2) and (3). The prefactor $M_0(T)$ and the in-plane upper critical field $H^{ab}_{c2}(T)$ are taken as fitting parameters, the best values of which are shown in the lower panel. By and large, the parameters behave as expected for $M_0 \propto 1/\lambda^2(T)$ and $H^{ab}_{c2}(T)$, although the low-$T$ value of 13 T for the maximum upper critical field is lower than $\approx 16$ T obtained from the resistivity data [3]. The limit $M_0(T \to 0) \approx 0.26$ G gives $\lambda^2(0)\gamma^{1/3} \sqrt{\gamma^2 - 1} \approx 2.1 \times 10^{-9}$ cm$^2$. Estimates of $\lambda(0)$ range between 110 nm [4] and 140 nm [4], which yield $\gamma \approx 6–9$.

In addition, our analysis of the field dependent resistivity of MgB$_2$ (following the procedure of Ref. [23] for polycrystalline superconductors) yields $\gamma \approx 6–9$ [23] in agreement with values extracted from CESR and M(H,T).

The agreement notwithstanding, one should exercise caution about the large anisotropy we extract from the magnetization data taken on powder samples. Our analysis of $M(H,T)$ disregards fluctuations of vortices, the reason being that MgB$_2$ does not seem to have a pronounced structure of weakly coupled superconducting layers, a prerequisite for strong fluctuations. Also, we take $M(H) \propto (H_{c2} - H)$ in the whole domain $H_{c2} < H < H^{ab}_{c2}$, too strong an assumption for anisotropies as large as $\gamma \approx 8$.

In conclusion, CESR shows a large distribution of $H_{c2}$ in high quality MgB$_2$ powders. These results, together with a detailed analysis of magnetization data are suggestive of a significant anisotropy of $H_{c2}$. If this is the case, magnetic field dependent experimental results on MgB$_2$ have to be reconsidered. A possible low minimum $H_{c2} < 2$ T has important consequences on the technical applications of this material. Nevertheless, single crystals are needed to definitely resolve the issue of anisotropy in MgB$_2$.

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FIG. 1. CESR linewidth versus temperature in MgB$_2$ powder at 9 GHz. The continuous curve is the resistance measured on a pressed pellet from the same batch as used for CESR. Inset: 9 GHz CESR spectrum at 500 K.

FIG. 2. CESR spectra of MgB$_2$ at various frequencies a) - c) in the normal state at 40 K; and d) -f) at T=5 K. The whole sample is superconducting at H=1.28 T and 5 K. Note the diamagnetic shift of the resonance with respect to the 40 K spectrum. Part of the sample is in the normal state at higher ESR frequencies, the superconducting component is marked by an arrow. Dashed and full lines below the experimental spectra are Lorentzian fits to the normal and superconducting CESR, respectively.

FIG. 3. Temperature dependence of the diamagnetic shift (full symbols are up, open symbols are down sweeps) of the CESR at 35 GHz (1.28 T) and diamagnetic magnetization measured by SQUID (solid curve) at 1.28 T.

FIG. 4. The upper panel shows the reversible magnetization $M(H)$ of the MgB$_2$ powder at temperatures from 6 to 34 K with a 2 K step. Solid lines are calculated with the help of Eqs. (2) and (3) with two fitting parameters $M_0$ and $H_{c2}^{ab}$. The latter are plotted in the lower panel.
1.28 T

$\Delta H_0$ (G)

$T$ (K)

$M$ (G)
