Anisotropy of Superconducting MgB_2 as Seen in Electron Spin Resonance and Magnetization Data

F. Simon, A. Jánossy, T. Fehér, and F. Murányi

Institute of Physics, Budapest University of Technology and Economics and Solids in Magnetic Fields Research Group of the Hungarian Academy of Sciences, P.O. Box 91, H-1521 Budapest, Hungary

S. Garaj and L. Forró

Department de Physique, Ecole Polytechnique Federal de Lausanne, CH-1015 Lausanne, Switzerland

C. Petrovic, S. L. Bud'ko, G. Lapertot,* V. G. Kogan, and P. C. Canfield

Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

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We observed the conduction electron spin resonance (CESR) in fine powders of MgB_2 both in the superconducting and normal states. The Pauli susceptibility is $\chi_s = 2.0 \times 10^{-5}$ 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 $H_{c2}^{ab}/H_{c2}^{c} \approx 6-9$.

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Following the recent discovery of superconductivity in MgB_2 [1] several of its fundamental properties have been established. MgB_2 is a type II superconductor with $\lambda \approx 140$ nm [2] and the upper critical field $H_{c2} \approx 16$ T [3]. 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 for both the basic understanding of this material and applications; it is enough to mention that the anisotropy strongly affects the pinning and critical currents.

An anisotropic or multicomponent superconducting gap was inferred from a number of indirect measurements and was suggested in several theoretical descriptions of MgB_2 [4–11]. For partially oriented crystallites, the anisotropy ratio is reported as $\gamma = H_{c2}^{ab}/H_{c2}^{c} = 1.73$ [12]; for c-axis oriented films $\gamma \approx 2$ [13] was found. In this Letter, we report estimates of the anisotropy parameter γ 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, χ_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 $H_{c2} \approx 16$ T [3]. The data suggest that H_{c2} of MgB_2 may be strongly anisotropic.

Isotopically pure $Mg^{11}B_2$ ($T_c = 39.2$ K) samples from the same batch as reported elsewhere [14] were used for the experiments. The original sample consisted of 100 μm large aggregates of small grains. The samples were ground in a mortar to crush the aggregates. Most of the resulting grains were between 0.5 and 5 μm in size and were separated by mixing into ESR silent vacuum grease or SnO_2. Crushing the aggregates increased the CESR 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 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 $CuSO_4 \cdot 5H_2O$. The 9 GHz spectrometer uses a resonant cavity and the so-called vortex noise generated by the field modulation prohibits ESR measurements in the superconducting state below the irreversibility line [15]. The high-field ESR spectrometer (Budapest HF-ESR lab, 35 GHz and higher frequencies) does not utilize a resonant cavity and 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 line shape characteristic of a relaxationally broadened ESR and homogeneous excitation (Fig. 1 inset). We find $g = 2.0019 \pm 0.0001$ for the g factor at 40 K at both 35

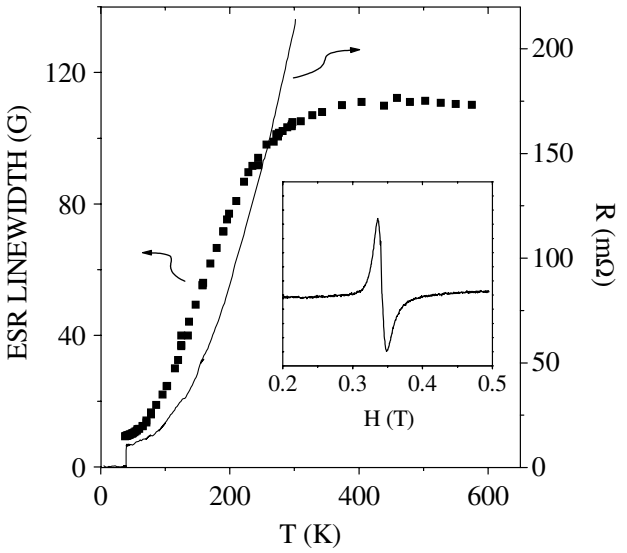

FIG. 1. CESR linewidth versus T in MgB_2 powder at 9 GHz. The solid curve is the resistance measured on a pressed pellet from the same batch as used for CESR. Inset: 9 GHz CESR spectrum at 500 K.

and 9 GHz. At 300 K and 9 GHz we get $g = 2.001 \pm 0.001$. The CESR intensity is T independent between 450 and 600 K and the spin susceptibility is $\chi_s = (2.0 \pm 0.3) \times 10^{-5}$ emu/mole. Assuming negligible electron-electron correlations, the density of states at the Fermi level is 0.6 states/eV in agreement with band structure calculations [16]. At lower T's, the size of larger grains ($s = 5\ \mu$m) becomes comparable or larger than the skin depth, $\delta = (\rho/\pi\mu_0 f)^{1/2}$, and the observed CESR intensity decreases. Here ρ denotes the specific resistivity of MgB_2, μ_0 is the vacuum permeability, and f is the ESR frequency. At 40 K, the ESR intensity is ~25% of the high-T value in agreement with the decrease in δ estimated from the resistance (Fig. 1). At 300 and 40 K the calculated skin depths at $f = 9$ GHz are $\delta = 1.6$ and 0.3 μm, using values of ρ for dense MgB_2 wires [17].

Below 400 K, deviations from the antisymmetric line shape appear. In most cases, a T dependent mixture of Lorentzian derivative absorption and dispersion components simulates well the observed line. Figure 1 shows the T dependence of the CESR linewidth in the normal state. The Lorentzian line shape is the signature of a homogeneous line broadening; in this case the half width at half maximum of the Lorentzian absorption line is $w = 1/\gamma_e T_1$, where T_1 is the spin-lattice relaxation time and γ_e is the electronic gyromagnetic factor. The electron mean free path, ℓ, is about 0.06 μm 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] $\delta_{\text{eff}} = 1/3 v_F (T_1 \tau)^{1/2} \approx 4\ \mu$m is comparable to the maximum grain size, 5 μm, and the conduction electron magnetization is homogeneous. There is a field dependent residual w at low T, followed by a strong increase with T and a broad maximum at 450 K. At 40 K and 9 GHz the line is narrow, $w = 15$ G. At 40 K and 225 GHz the line is inhomogeneous; it is broadened to about 35 G. The T dependent contribution to w is field independent.

As expected for a light metal [19], MgB_2 has a g factor of 2.0019 close to the free electron value of 2.0023 and a T dependent w (proportional to $1/T_1$) which follows the resistance below 200 K. However, the maximum in w observed in MgB_2 at 450 K has no analog 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 T's, and a T dependent diamagnetic shift in the field position of the resonance is observed (Figs. 2a and 2d). The line also broadens, but the broadening is roughly 3 times less than the shift. Below the irreversibility line ($T_{\text{irr}} = 31$ K at 1.28 T) the penetration of magnetic flux is hysteretic and the line position and width depend on the direction of the 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.

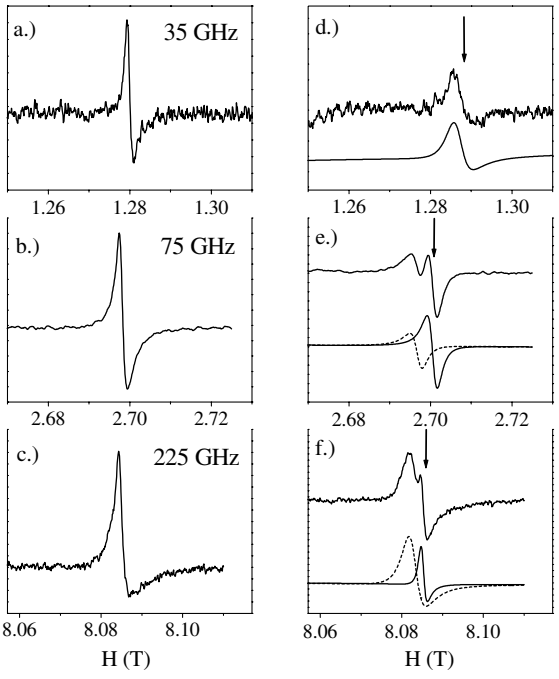

FIG. 2. CESR spectra of MgB_2 at various frequencies (a)–(c) in the normal state at 40 K and (d)–(f) at $T = 5$ K. The whole sample is superconducting at $H = 1.28$ T and 5 K. Note the diamagnetic shift of the resonance with respect to the 40 K spectrum. Part of the sample is in the normal state at higher 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.

Figure 3 shows the T dependence of the CESR shift, $\Delta H_0(T) = H_0(T) - H_0(40\ \mathrm{K})$, at 35 GHz, where $H_0(T)$ is the resonance field of the ESR spectra. It follows closely the field cooled (FC) magnetization $M(T)$ measured at 1.28 T by the SQUID magnetometer shown for comparison. The rough agreement of $\Delta H_0(T)$ and $4\pi|M(T)|$ and their similar T 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. [20] and references therein) only.

The complex line shape seen in Figs. 2e and 2f at higher fields is due to an inhomogeneous distribution of ΔH_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_3C_{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 μm) 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 up-shifted 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. 2d), i.e., T dependent diamagnetic shift and broadening below T_c. The value of ΔH_0 decreases with increasing field, following the decrease of the superconducting magnetization, and its values at $T = 2.5$ K are $\Delta H_0 = 25$, 9, and 5 G at 2.7, 5.4, and 8.1 T, respectively.

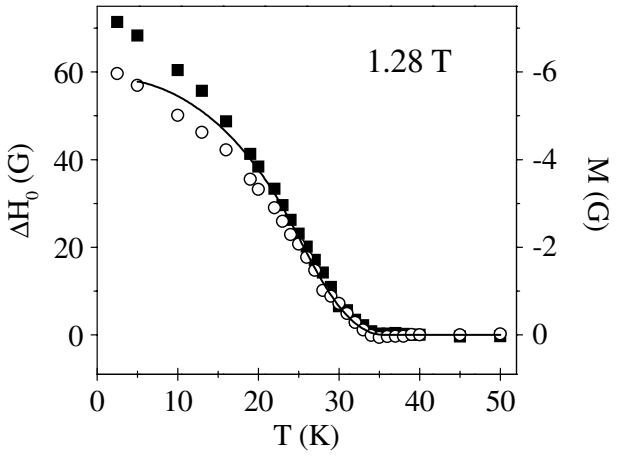

FIG. 3. T dependence of CESR shift (full symbols are up sweeps; open symbols are down sweeps) at 35 GHz (1.28 T) and FC magnetization measured at 1.28 T (solid curve).

Thus, the up-shifted line (Fig. 2) 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. As the applied field is increased, the CESR intensity of the superconducting fraction with respect to the intensity of the normal state fraction decreases (Figs. 2e and 2f). These observations provide evidence for a low value ($\sim$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 analyzing 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 $\gamma = H_{c2}^{ab}/H_{c2}^{c}$ placed in a field $\mathbf{H}$ along z. The distribution of grains over their c direction is given by $dN = N \sin\theta d\theta/2$ with θ being the angle between c and $\mathbf{H}$. The grain upper critical field depends on θ according to $H_{c2}(\theta) = H_{c2}^{ab}/\sqrt{\epsilon(\theta)}$ with $\epsilon = 1 + (\gamma^2 - 1)\cos^2\theta$.

In agreement with Ref. [12], we assume $H_{c2}^{ab} > H_{c2}^{c}$ ($\gamma > 1$) and consider the field domain $H_{c2}^{c} < H < H_{c2}^{ab}$ following the procedure of [22]. Clearly, only the grains with $H_{c2}(\theta) > H$ contribute to the superconducting M. The grain orientation θ_0, for which the given H is the upper critical field, is given by $\cos^2\theta_0 = [(H_{c2}^{ab}/H)^2 - 1]/(\gamma^2 - 1)$. We then have $M_z = \int_{\theta_0}^{\pi/2} M_z(\theta, H) \sin\theta\, d\theta$. According to Ref. [23], the magnetization of the grain θ near its H_{c2} is given by

$$-4\pi M_z = \frac{H_{c2}(\theta) - H}{2\kappa^2 \beta \gamma^{2/3}}\, \epsilon(\theta). \qquad (1)$$

Here, $\beta = 1.16$ and $\kappa \gg 1$. We then obtain

$$M_z = -M_0 f(h), \quad M_0 = \frac{\phi_0}{32\pi^2 \lambda^2 \beta \gamma^{1/3}\sqrt{\gamma^2 - 1}}, \qquad (2)$$

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

where $h = H/H_{c2}^{ab}$ and $\lambda = (\lambda_{ab}^2 \lambda_c)^{1/3}$ is the *average* penetration depth. It is seen that as $H \to H_{c2}^{ab}$, $M_z \propto (H_{c2}^{ab} - H)^{3/2}$; 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 T's, along with solid curves obtained by fitting the data to Eqs. (2) and (3). The prefactor $M_0(T)$ and $H_{c2}^{ab}(T)$ are

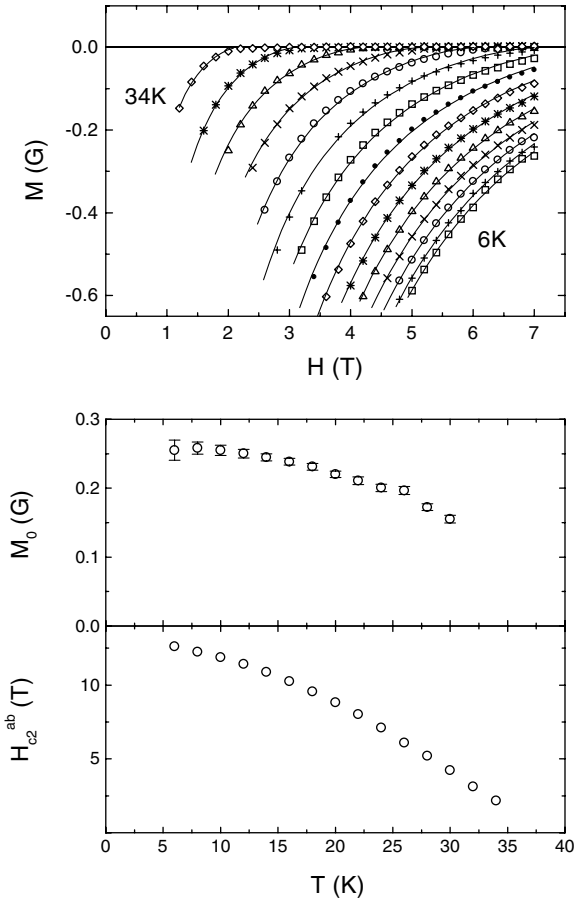

FIG. 4. The upper panel shows the reversible magnetization $M(H)$ of the MgB_2 powder at temperatures from 6 to 34 K with a 2 K step. Solid lines are calculated with the help of Eqs. (2) and (3) with two fitting parameters M_0 and H_{c2}^{ab}, shown in the lower panel.

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 $H_{c2}(T)$, although the low-T value of 13 T for the maximum H_{c2}^{ab} is below $\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 [24] and 140 nm [2], which yield $\gamma \approx 6$–9.

Still 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 $H_{c2}^{c} < H < H_{c2}^{ab}$, too strong an assumption for anisotropies as large as $\gamma \sim 8$.

In conclusion, CESR shows a large distribution of H_{c2} in high quality MgB_2 powders. These results, along with the analysis of magnetization data, are suggestive of a significant anisotropy of H_{c2}. A possible low minimum $H_{c2} \sim 2$ T has important implications for applications and physics of this material.

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*On leave from Commissariat à l'Energie Atomique, DRFMC-SPSMS, 38054 Grenoble, France.

[1] J. Nagamatsu *et al.,* Nature (London) **410**, 63 (2001).
[2] D. K. Finnemore *et al.,* Phys. Rev. Lett. **86**, 2420 (2001).
[3] S. L. Bud'ko *et al.,* Phys. Rev. B **63**, 220503 (2001).
[4] Y. Wang, T. Plackowski, and A. Junod, Physica (Amsterdam) **355C**, 179 (2001).
[5] F. Bouquet *et al.,* cond-mat/0104206.
[6] S. V. Shulga *et al.,* cond-mat/0103154.
[7] E. Bascones and F. Guinea, cond-mat/0103190.
[8] A. Y. Liu, I. I. Mazin, and J. Kortus, cond-mat/0103570.
[9] S. Haas and K. Maki, cond-mat/0104207.
[10] C.-T. Chen *et al.,* cond-mat/0104285.
[11] A. V. Pronin *et al.,* cond-mat/0104291.
[12] O. F. de Lima *et al.,* Phys. Rev. Lett. **86**, 5974 (2001).
[13] S. Patnaik *et al.,* Supercond. Sci. Technol. **14**, 315 (2001).
[14] S. L. Bud'ko *et al.,* Phys. Rev. Lett. **86**, 1877 (2001).
[15] A. Janossy and R. Chicault, Physica (Amsterdam) **192C**, 399 (1992).
[16] J. Kortus *et al.,* Phys. Rev. Lett. **86**, 4656 (2001).
[17] P. C. Canfield *et al.,* Phys. Rev. Lett. **86**, 2423 (2001).
[18] J. Winter, *Magnetic Resonance in Metals* (Clarendon Press, Oxford, 1970).
[19] Y. Yafet, Solid State Phys. **14**, 1 (1963).
[20] N. M. Nemes *et al.,* Phys. Rev. B **61**, 7118 (2000).
[21] P. G. de Gennes, Solid State Commun. **4**, 95 (1966).
[22] V. G. Kogan and J. R. Clem, Jpn. J. Appl. Phys. **26**, 1159 (1987).
[23] V. G. Kogan and J. R. Clem, Phys. Rev. B **24**, 2497 (1981).
[24] J. R. Thompson *et al.,* cond-mat/0103514.