Generalized Elliott-Yafet Theory of Electron Spin Relaxation in Metals: Origin of the Anomalous Electron Spin Lifetime in MgB_2

F. Simon,[1,*] B. Dóra,[1,2] F. Murányi,[1,+] A. Jánossy,[1] S. Garaj,[3,‡] L. Forró,[3] S. Bud'ko,[4] C. Petrovic,[4,§] and P. C. Canfield[4]

[1]*Budapest University of Technology and Economics, Institute of Physics and Condensed Matter Research Group of the Hungarian Academy of Sciences, H-1521 Budapest, Hungary*

[2]*Max-Planck-Institut für Physik Komplexer Systeme, Nöthnitzer Str. 38, 01187 Dresden, Germany*

[3]*Institute of Physics of Complex Matter, FBS Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland*

[4]*Ames Laboratory, U.S. Department of Energy and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*

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The temperature dependence of the electron-spin relaxation time in MgB_2 is anomalous as it does not follow the resistivity above 150 K; it has a maximum around 400 K and decreases for higher temperatures. This violates the well established Elliot-Yafet theory of spin relaxation in metals. The anomaly occurs when the quasiparticle scattering rate (in energy units) is comparable to the energy difference between the conduction and a neighboring bands. The anomalous behavior is related to the unique band structure of MgB_2 and the large electron-phonon coupling. The saturating spin relaxation is the spin transport analogue of the Ioffe-Regel criterion of electron transport.

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Knowledge of the electron-spin-lattice relaxation time, T_1, of conduction electrons plays a central role in assessing the applicability of metals for information processing using electron spin—spintronics [1]. T_1 is the time it takes for the conduction electron spin ensemble to relax to its thermal equilibrium magnetization after a nonequilibrium magnetization has been induced, e.g., by conduction electron-spin resonance (CESR) excitation [2] or by a spin-polarized current [1]. The Elliott-Yafet (EY) theory of T_1 in metals [3,4] has been well established in the past 50 years on various systems such as elemental [5] and one-dimensional [6] metals. It is based on the fact that the spin part of the conduction electron wave functions is not a pure Zeeman state but is an admixture of the spin up and down states due to spin-orbit (SO) coupling. As a result, momentum scattering due to phonons or impurities induces electron-spin-flip, which leads to spin relaxation. The relative weakness of the SO coupling results in $T_1 \gg \tau$ (τ being the momentum relaxation time) which explains the motivation behind the efforts devoted to the spintronics applications of metals.

A consequence of the EY theory is the so-called Elliott-relation, i.e., a proportionality between T_1 and τ [3]:

$$\frac{1}{T_1} = \alpha\left(\frac{L}{\Delta E}\right)^2 \frac{1}{\tau}. \quad (1)$$

Here α is a band structure dependent constant and for most elemental metals $\alpha \approx 1$–10 (Ref. [5]). L is the SO splitting for spin up and down electrons in a valence (or unoccupied) band near the conduction band with an energy separation of ΔE. E.g. in sodium, the conduction band is $3s$ derived, the relevant SO state is the $2p$ with $\Delta E = 30.6$ eV and $L = 0.16$ eV giving $(L/\Delta E)^2 = 2.7 \times 10^{-5}$ [4].

The Elliott-relation shows that the temperature dependent resistivity and CESR linewidth are proportional, the two being proportional to the inverse of τ and T_1, respectively. This enabled its experimental test for the above range of metals. Much as the Elliott-relation has been confirmed, it is violated in MgB_2 as therein the CESR linewidth and the resistivity are not proportional above 150 K [7].

Here, we study this anomaly using MgB_2 samples with different B isotopes and impurity concentrations and we show that the anomaly is intrinsic to MgB_2. We present an exact treatment of the SO scattering of conduction electrons in the presence of a nearby band with energy separation ΔE, by extending the Mori-Kawasaki formula developed for localized spins to itinerant electrons. The result shows that the Elliott-relation breaks down when ΔE is comparable to $\hbar/\tau$. Adrian deduced a similar result with a qualitative argument [8]. The role of ΔE is disregarded in the EY theory since typical values are $\Delta E \approx 10$ eV and $\hbar/\tau = 2\pi k_B T\lambda \approx 6$ meV at $T = 100$ K and $\lambda = 0.1$ electron-phonon coupling. We show that the occurrence of the anomaly in MgB_2 is related to the unique features in its band structure and the large electron-phonon coupling.

We performed CESR measurements on three kinds of fine powder MgB_2 with isotope pure ^{10}B, ^{11}B, and natural boron (20% ^{10}B and 80% ^{11}B). The samples have slightly different impurity content, shown by the varying residual CESR linewidth, ΔB_0. The temperature dependent T_1 and the CESR linewidth, ΔB, are related: $\Delta B = \Delta B_0 + 1/\gamma T_1$, where $\gamma/2\pi = 28$ GHz/T is the electron gyromagnetic factor. ESR spectroscopy was done on a Bruker X-band spectrometer (center field 0.33 T) in the 4–700 K temperature range on samples sealed under He in quartz tubes. The anomalous temperature dependence of ΔB or T_1

is independent of sample morphology, isotope content, or thermal history. ΔB is also independent of the magnetic field, apart from a small change in ΔB_0 [9]. Resistance and SQUID magnetometry on samples from the same batches show $RRR > 20$ and sharp (<0.5 K) superconducting transition, which attest the high sample quality. Heating the samples in the ESR measurement (about 1 h duration) to 700 K does not affect the superconducting properties.

We reported previously the anomalous temperature dependence of the CESR linewidth in $Mg^{11}B_2$: although the linewidth follows the resistance for the 40–150 K temperature range, it deviates above 150 K and saturates above 400 K [7]. This was confirmed independently [10,11]. To our knowledge, this is the only metal where such phenomenon is observed. We extended the previous measurement to 700 K and the result is shown in Fig. 1. Interestingly, the CESR linewidth does not just saturate at high temperatures, as found previously, but *decreases* above 500 K. The phenomenon is reversible upon cooling with no dependence on the thermal protocol and it is reproduced on several samples of different purity and boron isotopes; thus, it is intrinsic to MgB_2.

We explain the anomalous temperature dependence of T_1 in general before including the specifics of MgB_2. The EY theory disregards the magnitude of τ and takes lifetime effects only to lowest order into account [3,4]. The extended description involves the Kubo-formalism and is based on a two-band model Hamiltonian, $H = H_0 + H_{\mathrm{SO}}$, where

$$H_0 = \sum_{k,\nu,s} [\epsilon_\nu(k) + \hbar\gamma Bs] c^+_{k,\nu,s} c_{k,\nu,s} + H_{\mathrm{scatt}},$$
$$H_{\mathrm{SO}} = \sum_{k,\nu\neq\nu',s,s'} L_{s,s'}(k) c^+_{k,\nu,s} c_{k,\nu',s'}. \tag{2}$$

Here ν, $\nu' = 1$ or 2 are the band, s, s' are spin indices, $L_{s,s'}$ is the SO coupling, and B is the magnetic field along the z direction. H_{scatt} is responsible for the finite τ. The SO coupling does not split spin up and down states in the same band for a crystal with inversion symmetry; however, it joins different spin states in the two bands [1]. The Hamiltonian in Eq. (2) is essentially as that of Elliott treated by time-dependent perturbation [3] but we calculate T_1 from the Mori-Kawasaki formula [12,13]:

$$\frac{1}{T_1} = -\frac{1}{2\langle S_z\rangle} \mathrm{Im} G^R_{PP^+}(\omega_{\mathrm{L}}), \tag{3}$$

where $\langle S_z\rangle$ is the expectation value of the spin along the magnetic field, $\omega_{\mathrm{L}} = \gamma B$ is the Larmor frequency, and $G^R_{PP^+}(\omega)$ is the Fourier transform of

$$G^R_{PP^+}(t) = -i\Theta(t)\langle [P(t), P^+(0)]\rangle_{H_0}, \qquad \hbar P = [H_{\mathrm{SO}}, S^+]. \tag{4}$$

The expectation value in Eq. (4) is evaluated with the unperturbed Hamiltonian, H_0.

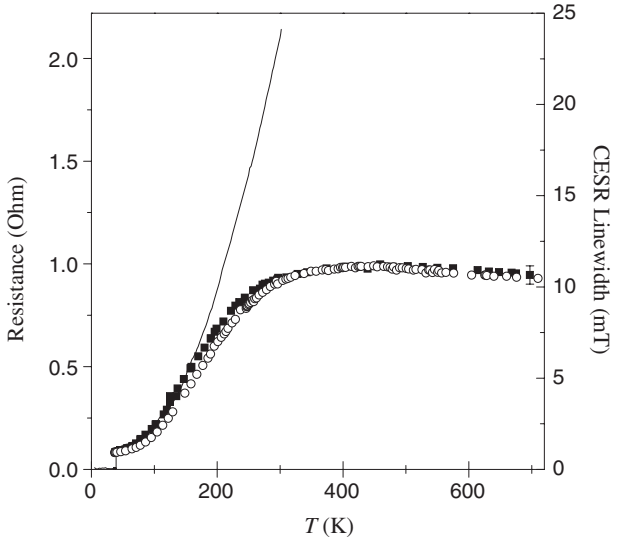

FIG. 1. Comparison of the temperature dependent CESR linewidth (■: $Mg^{11}B_2$, ○:MgB_2 of natural boron) and the resistance (solid curve) for $Mg^{11}B_2$. The two types of data overlap in the 40–150 K temperature range.

Assuming that the two bands are separated by $\Delta E(k) = \hbar\Delta\omega(k)$, a standard calculation yields [14]

$$\frac{1}{T_1} = \left\langle \frac{L_z^2(k_F) + 2|L_{\downarrow\uparrow}(k_F)|^2}{\hbar^2} \frac{\tau}{1 + (\Delta\omega(k_F)\tau)^2} \right\rangle, \tag{5}$$

where $\langle \ldots \rangle$ means a Fermi surface average, $L_z = L_{\uparrow,\uparrow} - L_{\downarrow,\downarrow}$, and we neglected the Larmor frequency as $\omega_{\mathrm{L}} \ll \Delta\omega(k_F)$. Equation (5) was deduced by Adrian using a qualitative argument, which involved an effective magnetic field, $L/\hbar\gamma$, fluctuating with τ correlation time [8].

We approximate Eq. (5) using effective values for the band-band energy separation and the SO coupling:

$$\frac{1}{T_1} = \frac{L^2_{\mathrm{eff}}}{\hbar^2} \frac{\tau}{1 + \Delta\omega^2_{\mathrm{eff}}\tau^2}. \tag{6}$$

This returns the Elliott-relation when $\tau\Delta\omega_{\mathrm{eff}} \gg 1$ and gives a decreasing spin relaxation rate with increasing τ^{-1} when $\tau\Delta\omega_{\mathrm{eff}} \leq 1$, thus it can be regarded as a generalization of the EY theory. We show below that it describes the spin relaxation in MgB_2.

Electronic properties of MgB_2 are described by the so-called two-band model meaning that the conduction bands related to boron σ and π bonds have different electron-phonon couplings, different affinity to defects, and that the interband momentum scattering is weaker than the intraband ones [15]. As a result, the conductivity is given by a parallel resistor formula [15]; i.e., the band with a longer τ dominates the transport. In contrast, the CESR spin relaxation is dominated by the band with *shorter* T_1. Although the interband momentum scattering time, $\tau_{\sigma\pi}$ is longer than the intraband momentum scattering times, τ_σ and τ_π, it is still much shorter than T_1. Thus an electron is scattered back and forth between the two types of bands

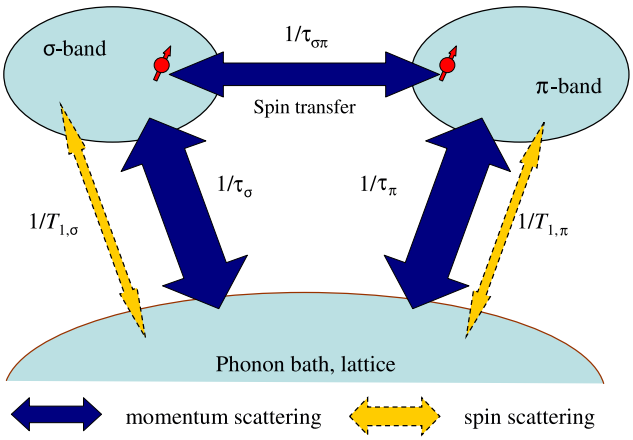

FIG. 2 (color online). Schematics of the spin-lattice relaxation in MgB_2 in the two-band model framework. The arrow thicknesses represent the relaxation rates (not to scale). Note that the interband momentum scattering rate is larger than the spin-lattice relaxation rates; therefore, there is a spin transfer between the two types of bands.

several times before flipping its spin, which is depicted in Fig. 2. The overall T_1^{-1} is the average of the spin-lattice relaxation rates weighted by the relative DOS on the σ and π bands, $N_\pi = 0.56$ and $N_\sigma = 0.44$ [16]:

$$\frac{1}{T_1} = \frac{N_\pi}{T_{1,\pi}} + \frac{N_\sigma}{T_{1,\sigma}}. \quad (7)$$

In Fig. 3, we show the band structure of MgB_2 from Refs. [17,18] near the Fermi energy. Two boron σ and two π bands cross the Fermi energy such that the π bands are separated from other bands with $\Delta E_\pi \geq 2$ eV whereas the two σ bands are close to each other and $\Delta E_\sigma \approx 0.2$ eV. Based on the above theory and Eq. (6), we conclude that T_1 follows the EY mechanism for the π bands, whereas it is described by the novel mechanism for the σ bands. With this in mind and the two-band model result of Eq. (7), the CESR linewidth is

$$\Delta B = \Delta B_0 + \frac{1}{\gamma\hbar^2}\left(\frac{N_\pi L_{\mathrm{eff},\pi}^2}{\Delta\omega_{\mathrm{eff},\pi}^2}\frac{1}{\tau_\pi} + \frac{N_\sigma L_{\mathrm{eff},\sigma}^2 \tau_\sigma}{1+\Delta\omega_{\mathrm{eff},\sigma}^2\tau_\sigma^2}\right), \quad (8)$$

where we introduced band indices. We calculate τ with the Debye-model assuming zero residual scattering:

$$\frac{1}{\tau_n} = \frac{2\pi k_B T \lambda_{\mathrm{tr},n}}{\hbar}\int_0^{\omega_D}\frac{d\Omega}{\Omega}\left(\frac{\Omega}{\omega_D}\right)^4\left[\frac{\hbar\Omega/k_B T}{\sinh\frac{\hbar\Omega}{2k_B T}}\right]^2, \quad (9)$$

where $n = \sigma, \pi$, ω_D is the Debye frequency, and $\lambda_{\mathrm{tr},n}$ are the transport electron-phonon couplings from Ref. [15] containing both intra- and interband scattering.

In Fig. 4, we show ΔB for $Mg^{11}B_2$ and $Mg^{10}B_2$ between 40 and 700 K and the calculated values using Eq. (8) with parameters in Table I obtained from a fit. The larger residual linewidth in the ^{10}B ($\Delta B_0 = 2$ mT) than in the ^{11}B sample ($\Delta B_0 = 1$ mT) is related to a larger defect

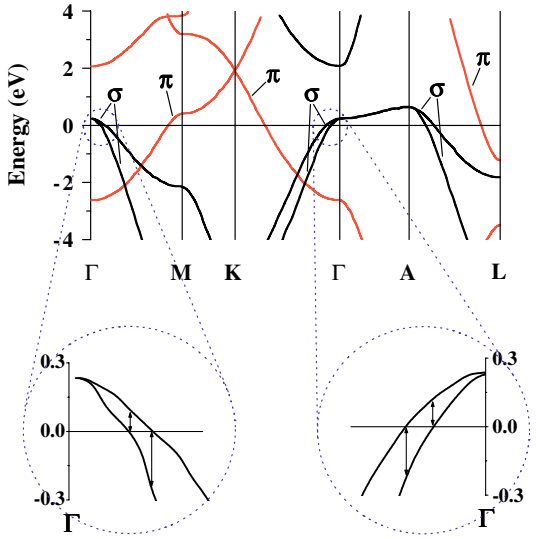

FIG. 3 (color online). Band structure of MgB_2 near the Fermi energy after Refs. [17,18]. Two of the σ bands (black) cross the Fermi surface close to each other near the Γ and A points, whereas π bands (red) are separated from other bands with a larger optical gap at the crossing. We show the dispersion with 8 times larger wave-vector resolution near the Γ points with arrows for possible ΔE_σ values. Reprinted with permission from Refs. [17,18], Kortus *et al.*, Phys. Rev. Lett. **86**, 4656 (2001) and N. I. Medvedeva *et al.*, Phys. Rev. B **64**, 020502(R) (2001).

concentration in the starting boron, the preparation method and the starting Mg being identical. Apart from this, the only difference between the two samples is the different Debye temperature, Θ_D. The calculated ΔB (solid curves)

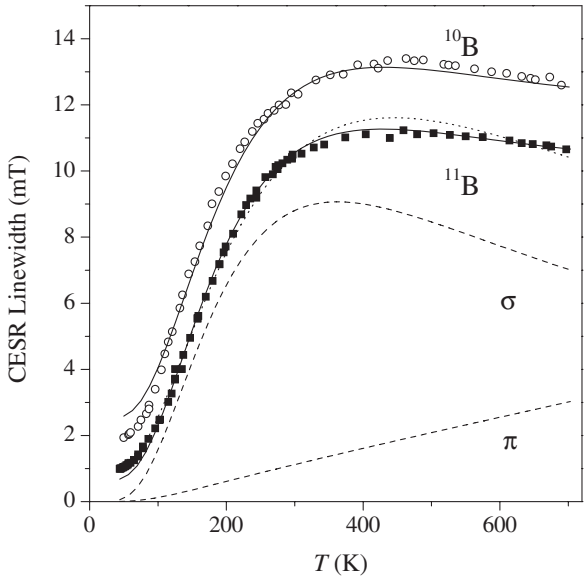

FIG. 4. Measured and calculated (solid curves) ΔB in MgB_2 with ^{11}B and ^{10}B. Note the larger residual linewidth in the latter sample. Dashed curves show contributions from the σ and π bands separately. Dotted curve shows a calculation for the the ^{11}B sample assuming T_1^{-1} is due to σ bands only.

TABLE I. Parameters used to calculate the CESR linewidth in MgB_2. Standard deviations indicate free parameters of the fit.

λ_{tr} [15]		L_{eff} (meV)		ΔE_{eff} (eV)		Θ_D (K)	
σ	π	σ	π	σ	π	^{11}B	^{10}B
1.09	0.46	0.64(2)	2.8(1)	0.194(5)	2	535(15)	555(15)

reproduces well the experimental data. The dotted curve in Fig. 4 is a calculation assuming that relaxation is given by the σ bands alone, which accounts relatively well for the data with three free parameters (L_σ, $\Delta E_{eff,\sigma}$, and ΔB_0). However, it fails to reproduce the slope of ΔB at higher temperatures, which shows the need to include relaxation due to the π bands.

The determination of $\Delta E_{eff,\sigma} \approx 0.2$ eV is robust as it is given by the temperature where the maximal ΔB is attained and its value is close to values expected from the band structure (arrows in Fig. 3). Knowledge of $\Delta E_{eff,\sigma}$ allows to determine the SO splitting independently, $L_{eff,\sigma} = 0.64$ meV, as usually only the $L/\Delta E$ ratio is known. The SO splitting for the atomic boron $2p$ orbital is $L = 0.23$ meV (Ref. [4]), which is in a reasonable agreement with the experimental value. ΔE_π was fixed to 2 eV which affects $L_{eff,\pi}$ as these are not independent. The isotope effect on Θ_D is $^{10}\Theta_D/^{11}\Theta_D = 1.04$, that is close to the expected $\sqrt{11/10}$ ratio. The Θ_D values are in agreement with the 440–1050 K values in the literature, which scatter depending on the experimental method [19,20]. The model could be improved by considering the Einstein model of phonons and the accurate band structure.

Finally, we note that the maximum of T_1^{-1} occurs when $\tau\Delta\omega \approx 1$. This coincides with the Ioffe-Regel criterion for the electron transport [21] when band-band separation is comparable to the bandwidth, w. For MgB_2, $w \approx 10$ eV [17] therefore saturation of the linewidth is not accompanied by a saturation of electrical resistivity.

In conclusion, we explain the anomalous spin-lattice relaxation in MgB_2 by extending the Elliott-Yafet theory to the case of rapid momentum scattering and near lying bands. The anomaly does not occur in conventional metals, which have small electron-phonon coupling and well separated bands. The band structure of some of the other diborides in, e.g., BeB_2 and CaB_2 predicts [18] similar phenomena but conventional spin relaxation in AlB_2, ScB_2, and YB_2. We predict that the effect is sensitive to pressure as this shifts the σ bands [22].

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*Corresponding author.
simon@esr.phy.bme.hu
[+]Present address: University of Zürich, Physics Institute, Winterthurerstr. 190, CH-8057 Zürich, Switzerland.
[‡]Present address: Harvard University, Department of Physics 17 Oxford Street, Cambridge, MA 02138, USA.
[§]Present address: Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA.

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