

## Generalized Elliott-Yafet Theory of Electron Spin Relaxation in Metals: Origin of the Anomalous Electron Spin Lifetime in MgB<sub>2</sub>

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The temperature dependence of the electron-spin relaxation time in MgB<sub>2</sub> 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 Elliott-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<sub>2</sub> 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  $T_1 \gg \tau$  ( $\tau$  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  $\tau$  [3]:

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

Here  $\alpha$  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  $\Delta E$ . 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  $\tau$  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<sub>2</sub> as therein the CESR linewidth and the resistivity are not proportional above 150 K [7].

Here, we study this anomaly using MgB<sub>2</sub> samples with different B isotopes and impurity concentrations and we show that the anomaly is intrinsic to MgB<sub>2</sub>. We present an exact treatment of the SO scattering of conduction electrons in the presence of a nearby band with energy separation  $\Delta E$ , by extending the Mori-Kawasaki formula developed for localized spins to itinerant electrons. The result shows that the Elliott-relation breaks down when  $\Delta E$  is comparable to  $\hbar/\tau$ . Adrian deduced a similar result with a qualitative argument [8]. The role of  $\Delta E$  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<sub>2</sub> 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<sub>2</sub> with isotope pure <sup>10</sup>B, <sup>11</sup>B, and natural boron (20% <sup>10</sup>B and 80% <sup>11</sup>B). The samples have slightly different impurity content, shown by the varying residual CESR linewidth,  $\Delta B_0$ . The temperature dependent  $T_1$  and the CESR linewidth,  $\Delta B$ , 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  $\Delta B$  or  $T_1$

is independent of sample morphology, isotope content, or thermal history.  $\Delta B$  is also independent of the magnetic field, apart from a small change in  $\Delta B_0$  [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  $\text{Mg}^{11}\text{B}_2$ : 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  $\text{MgB}_2$ .

We explain the anomalous temperature dependence of  $T_1$  in general before including the specifics of  $\text{MgB}_2$ . The EY theory disregards the magnitude of  $\tau$  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,  $H = H_0 + H_{\text{SO}}$ , where

$$\begin{aligned} H_0 &= \sum_{k,\nu,s} [\epsilon_\nu(k) + \hbar\gamma Bs] c_{k,\nu,s}^+ c_{k,\nu,s} + H_{\text{scatt}}, \\ H_{\text{SO}} &= \sum_{k,\nu \neq \nu',s,s'} L_{s,s'}(k) c_{k,\nu,s}^+ c_{k,\nu',s'}. \end{aligned} \quad (2)$$

Here  $\nu, \nu' = 1$  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.  $H_{\text{scatt}}$  is responsible for the finite  $\tau$ . 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]:

$$\frac{1}{T_1} = -\frac{1}{2\langle S_z \rangle} \text{Im} G_{PP^+}^R(\omega_L), \quad (3)$$

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

$$G_{PP^+}^R(t) = -i\Theta(t)\langle [P(t), P^+(0)] \rangle_{H_0}, \quad \hbar P = [H_{\text{SO}}, S^+]. \quad (4)$$

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

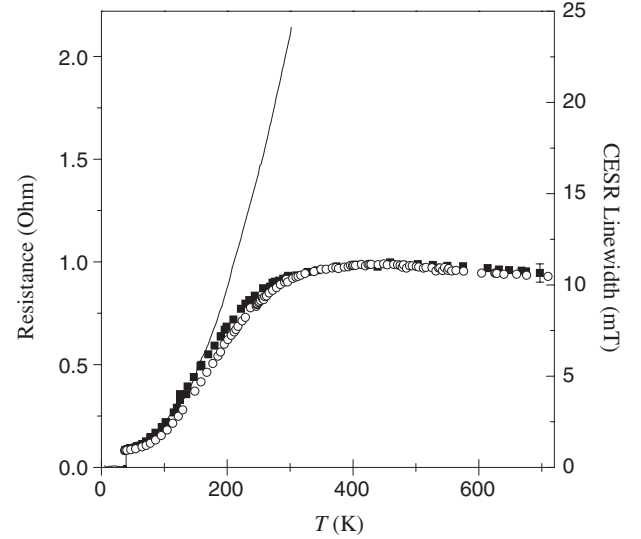


FIG. 1. Comparison of the temperature dependent CESR linewidth (■:  $\text{Mg}^{11}\text{B}_2$ , ○:  $\text{MgB}_2$  of natural boron) and the resistance (solid curve) for  $\text{Mg}^{11}\text{B}_2$ . The two types of data overlap in the 40–150 K temperature range.

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

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

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

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

$$\frac{1}{T_1} = \frac{L_{\text{eff}}^2}{\hbar^2} \frac{\tau}{1 + \Delta\omega_{\text{eff}}^2 \tau^2}. \quad (6)$$

This returns the Elliott-relation when  $\tau\Delta\omega_{\text{eff}} \gg 1$  and gives a decreasing spin relaxation rate with increasing  $\tau^{-1}$  when  $\tau\Delta\omega_{\text{eff}} \leq 1$ , thus it can be regarded as a generalization of the EY theory. We show below that it describes the spin relaxation in  $\text{MgB}_2$ .

Electronic properties of  $\text{MgB}_2$  are described by the so-called two-band model meaning that the conduction bands related to boron  $\sigma$  and  $\pi$  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  $\tau$  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,  $\tau_\sigma$  and  $\tau_\pi$ , it is still much shorter than  $T_1$ . Thus an electron is scattered back and forth between the two types of bands

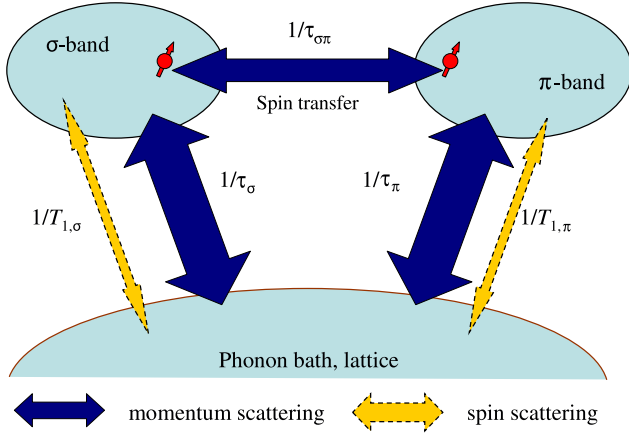


FIG. 2 (color online). Schematics of the spin-lattice relaxation in  $\text{MgB}_2$  in the two-band model framework. The arrow thicknesses represent the relaxation rates (not to scale). Note that the interband momentum scattering rate is larger than the spin-lattice relaxation rates; therefore, there 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  $\sigma$  and  $\pi$  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  $\text{MgB}_2$  from Refs. [17,18] near the Fermi energy. Two boron  $\sigma$  and two  $\pi$  bands cross the Fermi energy such that the  $\pi$  bands are separated from other bands with  $\Delta E_\pi \geq 2$  eV whereas the two  $\sigma$  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  $\pi$  bands, whereas it is described by the novel mechanism for the  $\sigma$  bands. With this in mind and the two-band model result of Eq. (7), the CESR linewidth is

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

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

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

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

In Fig. 4, we show  $\Delta B$  for  $\text{Mg}^{11}\text{B}_2$  and  $\text{Mg}^{10}\text{B}_2$  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  $^{10}\text{B}$  ( $\Delta B_0 = 2$  mT) than in the  $^{11}\text{B}$  sample ( $\Delta B_0 = 1$  mT) is related to a larger defect

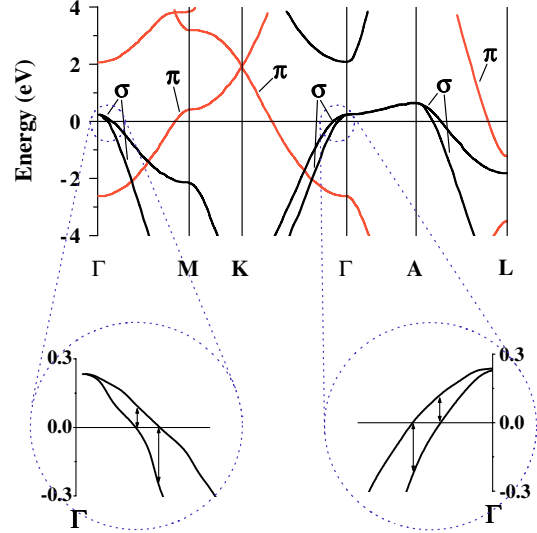


FIG. 3 (color online). Band structure of  $\text{MgB}_2$  near the Fermi energy after Refs. [17,18]. Two of the  $\sigma$  bands (black) cross the Fermi surface close to each other near the  $\Gamma$  and A points, whereas  $\pi$  bands (red) are separated from other bands with a larger optical gap at the crossing. We show the dispersion with 8 times larger wave-vector resolution near the  $\Gamma$  points with arrows for possible  $\Delta E_\sigma$  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,  $\Theta_D$ . The calculated  $\Delta B$  (solid curves)

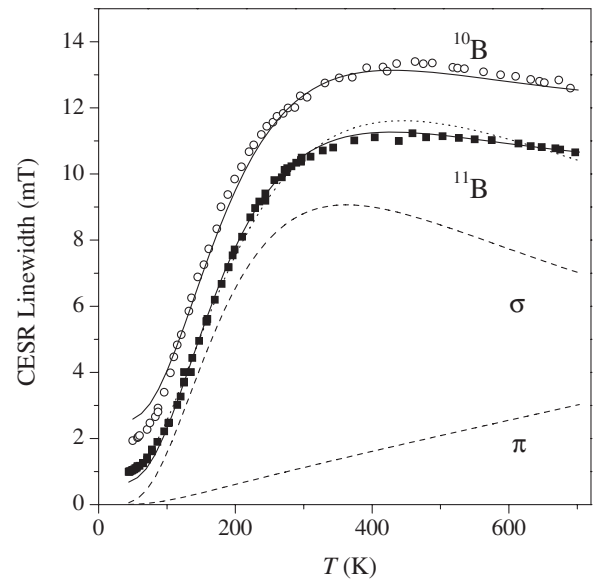


FIG. 4. Measured and calculated (solid curves)  $\Delta B$  in  $\text{MgB}_2$  with  $^{11}\text{B}$  and  $^{10}\text{B}$ . Note the larger residual linewidth in the latter sample. Dashed curves show contributions from the  $\sigma$  and  $\pi$  bands separately. Dotted curve shows a calculation for the the  $^{11}\text{B}$  sample assuming  $T_1^{-1}$  is due to  $\sigma$  bands only.

TABLE I. Parameters used to calculate the CESR linewidth in MgB<sub>2</sub>. Standard deviations indicate free parameters of the fit.

$\lambda_{\text{tr}}$ [15]		$L_{\text{eff}}$ (meV)		$\Delta E_{\text{eff}}$ (eV)		$\Theta_{\text{D}}$ (K)	
$\sigma$	$\pi$	$\sigma$	$\pi$	$\sigma$	$\pi$	<sup>11</sup> B	<sup>10</sup> 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  $\sigma$  bands alone, which accounts relatively well for the data with three free parameters ( $L_{\sigma}$ ,  $\Delta E_{\text{eff},\sigma}$ , and  $\Delta B_0$ ). However, it fails to reproduce the slope of  $\Delta B$  at higher temperatures, which shows the need to include relaxation due to the  $\pi$  bands.

The determination of  $\Delta E_{\text{eff},\sigma} \approx 0.2$  eV is robust as it is given by the temperature where the maximal  $\Delta B$  is attained and its value is close to values expected from the band structure (arrows in Fig. 3). Knowledge of  $\Delta E_{\text{eff},\sigma}$  allows to determine the SO splitting independently,  $L_{\text{eff},\sigma} = 0.64$  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.  $\Delta E_{\pi}$  was fixed to 2 eV which affects  $L_{\text{eff},\pi}$  as these are not independent. The isotope effect on  $\Theta_{\text{D}}$  is  $^{10}\Theta_{\text{D}}/^{11}\Theta_{\text{D}} = 1.04$ , that is close to the expected  $\sqrt{11/10}$  ratio. The  $\Theta_{\text{D}}$  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<sub>2</sub>,  $w \approx 10$  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<sub>2</sub> 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<sub>2</sub> and CaB<sub>2</sub> predicts [18] similar phenomena but conventional spin relaxation in AlB<sub>2</sub>, ScB<sub>2</sub>, and YB<sub>2</sub>. We predict that the effect is sensitive to pressure as this shifts the  $\sigma$  bands [22].

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