Generalized Elliott-Yafet Theory of Electron Spin Relaxation in Metals: Origin of the Anomalous Electron Spin Lifetime in MgB$_2$

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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.

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 $\tau$ [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$_2$ 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 $\Delta E$, 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 $\hbar/\tau = 2\pi k_B T \lambda = 6$ 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, $\Delta B_0$. 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 \( \Delta B_0 \) \cite{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 \cite{7}. This was confirmed independently \cite{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 Mg\(_2\)B\(_2\).

We explain the anomalous temperature dependence of \( T_1 \) in general before including the specifics of Mg\(_2\)B\(_2\). The EY theory disregards the magnitude of \( \tau \) and takes lifetime effects only to lowest order into account \cite{3,4}. The extended description involves the Kubo-formalism and is based on a two-band model Hamiltonian, \( H = H_0 + H_{SO} \), where

\[
H_0 = \sum_{k,v,s} \left[ \epsilon_v(k) + \hbar \gamma Bs \right] c_{k,v,s}^+ c_{k,v,s} + H_{\text{scatt}},
\]

\[
H_{SO} = \sum_{k,v,s,s'} L_{s,s'}(k) c_{k,v,s}^+ c_{k,v',s'}.
\]  

(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 \cite{1}. The Hamiltonian in Eq. (2) is essentially that of Elliott treated by time-dependent perturbation \cite{3,5} but we calculate \( T_1 \) from the Mori-Kawasaki formula \cite{12,13}:

\[
\frac{1}{T_1} = \frac{1}{2}\langle S_z \rangle \text{Im}G_{pp'}^{R}(\omega_L),
\]  

(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

\[
G_{pp'}^{R}(t) = -i\Theta(t)\langle [P(t), P^+(0)] \rangle_{H_0}, \quad \hbar P = [H_{SO}, S^+].
\]  

(4)

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

$$
\frac{1}{T_1} = \frac{N_\sigma}{T_{1,\sigma}} + \frac{N_\pi}{T_{1,\pi}}.
$$

In Fig. 3, we show the band structure of 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 $\Delta E_\pi \approx 2$ 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

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

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

$$
\frac{1}{\tau_n} = \frac{2\pi k_B T \lambda_{\text{tr},n}}{\hbar} \int_{\omega_0}^{\omega_D} d \Omega \frac{\Omega}{\omega_D} \left[ \frac{\hbar \Omega / k_B T}{\sinh(\hbar \Omega / 2k_B T)} \right]^2,
$$

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 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 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)
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 $\Delta E_{\text{eff},\sigma} = 0.2$ eV is robust as it is given by the temperature where the maximal $L$ 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 2$p$ 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 $\Theta_{D}$ is $10^{\Theta_{D}/11^{\Theta_{D}} = 1.04}$, that is close to the expected $\sqrt{11}/10$ ratio. The $\Theta_{D}$ 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 $\tau\Delta \omega = 1$. This coincides with the Ioffe-Regel criterion for the electron transport [21] when band-band separation is comparable to the bandwidth, $w$. For MgB$_{2}$, $w = 10$ 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 $\sigma$ bands [22].

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