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Unusual diffusive effects on the ESR of Nd$^{3+}$ ions in the tunable topologically nontrivial semimetal YBiPt

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Abstract
Electron spin resonance (ESR) of diluted Nd$^{3+}$ ions in the topologically nontrivial semimetallic (TNSM) YBiPt compound is reported. The cubic YBiPt compound is a non-centrosymmetric half Heusler material which crystallizes in the F43m space group. The low temperature Nd$^{3+}$ ESR spectra showed a $g$-value of 2.66(4) corresponding to a $\Gamma_6$ cubic crystal field Kramers’ doublet ground state. Remarkably, the observed metallic and diffusive (Dysonian) Nd$^{3+}$ lineshape presented an unusual dependence with grain size, microwave power, Nd$^{3+}$ concentration and temperature. Moreover, the spin dynamic of the localized Nd$^{3+}$ ions in YBiPt was found to be characteristic of a phonon-bottleneck regime. It is claimed that, in this regime for YBiPt, phonons are responsible for mediating the diffusion of the microwave energy absorbed at resonance by the Nd$^{3+}$ ions to the thermal bath throughout the skin depth ($\delta \approx 15 \mu m$). We argue that this is only possible because of the existence of highly mobile conduction electrons inside the skin depth of YBiPt that are strongly coupled to the phonons by spin–orbit coupling. Therefore, our unexpected ESR results point to a coexistence of metallic and insulating behaviors within the skin depth of YBiPt. This scenario is discussed in the light of the TNSM properties of this compound.

Keywords: topological materials, electron spin resonance, half-Heusler compound

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(Some figures may appear in colour only in the online journal)

1. Introduction
The recognition of a new quantum state of matter in topological insulating (TI) materials has recently attracted a great deal of attention from the condensed matter scientific community [1–5]. Nontrivial topological invariants in gapped bulk electronic bands yield robust gapless conducting states on the surface (edges) of these materials. Such conducting states protected by time-reversal symmetry emerge as consequence of an inverted band gap due to strong spin–orbit (SO) coupling [6, 7]. Moreover, the underlying physics of these materials is intimately connected to the quantum spin Hall effects (QSHE) [1, 8]. Quantum wells of HgTe/CdTe [9, 10] were confirmed as a bi-dimensional (2D) TI material. Yet Bi$_{1-x}$Sb$_x$ alloys [11, 12] and the tetradymite semiconductors such as Bi$_2$S$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ [13–15] are considered 3D TIs. A distinct class called topological crystalline insulators (TCI) [16] is realized in SnTe [17] and Pb$_{1-x}$Sn$_x$Se [18]. In this
specific case, the surface metallic states with locked spin and momentum are protected by structural crystalline symmetries rather than the time-reversal one. Besides these well-established TIs and TCIs, some Kondo insulator compounds, such as YbBiPt [19–21], SmB6 [22–27] and YbB6 [28] were also recently suggested as topological Kondo insulators (TKI). It is worth emphasizing that strong SO coupling is a crucial ingredient in all of these materials [20, 29, 30].

In particular, for the rare earth (RE) series of non-centrosymmetric half Heusler ternary semiconducting/semimetallic REBiPt compounds, first principle calculations predict band inversion in many members of this family. The topological (gapless) metallic surface states may emerge by either applying strain or chemical pressure [19, 31, 32]. These materials behave as small gap semiconductors ($\Delta \gtrsim 10$ meV) in the bulk with robust protected metallic states on the surface due to their strong SO coupling and nontrivial $Z_2$ topology [19, 31, 32].

Among the REBiPt compounds, YbBiPt has gained distinguished attention as a nontrivial topological semimetal due to its unusual transport properties [33] and the presence of conducting surface states [34]. Despite still being controversial [35], superconductivity with transition temperature $T_c \approx 0.77$ K has been reported for YbBiPt [34, 36]. Regardless of its inconclusive nature, the superconducting phase associated with nontrivial topology of the electronic bands might, in principle, create a propitious framework to investigate the putative surface states known as Majorana fermions [4, 37, 38].

Electron spin resonance (ESR) of diluted REs is a powerful local technique that can directly probe the nature of the interactions between localized magnetic moments and their electronic environment as well as the local, dynamic and static, crystalline site symmetry [39–41]. Therefore, ESR may be a suitable tool to investigate the robust metallic states in topologically nontrivial materials. In this regard, our research group studied the crystalline electric field (CEF) effects of diluted REs (Nd$^{3+}$, Gd$^{3+}$ and Er$^{3+}$) in Y$_{1-x}$RE$_x$BiPt about 15 years ago [42, 43]. At that time, we found an intriguing and anomalous Nd$^{3+}$ ESR lineshape behavior in Y$_{1-x}$Nd$_x$BiPt, which has not been reported because its nature was unrelated to CEF effects. Nonetheless, enlightened by the advent of TI materials and their astonishing physical properties recently discovered in these systems, we revisited this new subject and carried out new ESR experiments in order to elucidate the origin of such unusual lineshape behavior.

Therefore, in this work we report a detailed ESR investigation of the Nd$^{3+}$ lineshape in Y$_{1-x}$Nd$_x$BiPt (0.002 $\lesssim x \lesssim 0.10$). Our results provide important evidence of highly mobile (Dirac-like) conduction electrons (ce) strongly coupled, via SO-coupling, to the phonons within the microwave skin depth of YBiPt. Our main findings are: (i) coexistence of metallic and insulating behaviors (i.e. low carrier semimetallic behavior) within a microwave skin depth of $\delta \approx 15$ $\mu$m (considered a bulk measurement in conventional metallic systems [40, 41]); (ii) unusual microwave power, particle size, Nd$^{3+}$ concentration and temperature dependence revealed by spectral analysis; and (iii) occurrence of a phonon-bottleneck relaxation process in Nd$^{3+}$ doped YBiPt. All these features are discussed in light of the topologically nontrivial semimetallic (TNSM) properties of this compound.

2. Experimental details

Several batches of Y$_{1-x}$Nd$_x$BiPt (0.002 $\lesssim x \lesssim 0.10$) were synthesized using the self-flux technique [44] with starting composition ($1-x$)Y$_2$Nd$_1$Pt$_2$Bi$_2$. High-purity (99.99%°) RE elements from Ames have been used. The crucible containing the elements was placed in a quartz tube sealed in vacuum and slowly heated up to 1170 °C. After being kept at this temperature for 2h, the tube was cooled down to 900 °C with a rate of 10 °C h$^{-1}$. The collected crystals have as-grown planes with dimensions up to $4 \times 4$ mm$^2$. X-ray powder diffraction was used to verify the cubic crystalline structure and F43 m space group of YbBiPt.

The x-band ($\nu \approx 9.4$ GHz) ESR experiments were carried out in a conventional CW Bruker-ELEXSYS 500 spectrometer using 100kHz magnetic field modulation and a TE$_{102}$ cavity coupled to an Oxford helium gas flow system and a quartz/stainless steel cold tail liquid helium dewar. The ESR spectra were taken between $\approx$2 $\mu$W and $\approx$200 mW of microwave power. The 1.6 K ESR spectra were performed in a conventional Varian ESR spectrometer using a TE$_{102}$ cavity. The sample temperature was controlled using a quartz tail dewar for pumped liquid-helium bath experiments. To verify the appropriate performance of our AFC circuitry in the microwave power dynamic range, we have carried out ESR experiments of Er doped Au under the same experimental conditions used in this work (see figure 1 of supplementary information, stacks.iop.org/JPhysCM/28/125601/mmedia).

All ESR experiments were performed on gently powdered Y$_{1-x}$Nd$_x$BiPt single crystals with 0.002 $\lesssim x \lesssim 0.10$ and selected grain sizes within $\approx$100 $\mu$m to $\approx$2mm. The average ratio between grain size and skin depth is $\lambda = d / \delta \gtrsim 6.6$. The skin depth $\delta = (\mu / (2 \mu_0) \mu_0)^{1/2} \approx 15$ $\mu$m was estimated taking into account $\nu = 9.4$ GHz and the resistivity value of YBiPt at low-$T$ from [34]. We should mention here that at 10% Nd impurity doping the overall T dependence of the resistivity behavior remains similar to the undoped YBiPt. One can only observe a slight change in the residual resistivity, which is basically comparable with that found for crystals of the same compound coming from distinct batches. It should be mentioned that this level of doping is still away from the percolation limit if one considers the cubic crystalline structure symmetry.

3. Experimental results

First of all it is reasonable and quite convenient to introduce here the framework necessary to analyze the ESR lineshape behavior in Y$_{1-x}$Nd$_x$BiPt. It is well known that the microwave electromagnetic field is attenuated on the surface of metals due to their high conductivity. Thus, the microwave only penetrates the material up to a small length scale called skin depth, $\delta$, which is usually much smaller than the sample
dimensions. This fact leads to a vertically asymmetric ESR lineshape named Dysonian (figure 1(a)) [45]. In a metal, a local moment spin system has a very fast relaxation process which allows the resonating spins to transfer the absorbed microwave energy to the lattice very rapidly via exchange interaction with the ce. As such, the ESR signal intensity (doubly integrated ESR spectrum) usually increases linearly as a function of (microwave power)1/2 at a given temperature, as illustrated in figure 1(b). In contrast, the resonating spins present a symmetric ESR lineshape called Lorentzian when the microwave goes through the entire volume of an insulating material, as shown in figure 1(c). As the insulating materials are free of ce, the relaxation mechanism is dominated by phonons which are much slower than those in a metal. As a consequence, the ESR signal intensity in an insulator can saturate at high microwave power when the population of the spin levels, split by the Zeeman effect, tends to be equal at a given temperature. This effect is displayed in figure 1(d).

In fact, the overall ESR lineshape in a metallic environment is usually analyzed by the well accepted approach given by Dyson’s theory. In particular, the ESR lineshape for the microwave absorption at resonance by a localized magnetic ion is described in the diffusionless limit, 1 ≲ A/B ≲ 2.6 → T_D/T_2 ≫ 1 [45, 47], where T_D is the average time that a resonant spin takes to diffuse across the skin depth and T_2 is the spin–spin relaxation time. Within this limit, Dyson’s theory can be approximately simulated by a simple admixture of absorption and dispersion of Lorentzian lineshapes [48] with the A/B ratio changing monotonically from A/B ≈ 1 to A/B ≈ 2.6 for sample size d smaller and larger than δ, respectively [45, 47–49]. Nonetheless, this simple and fortuitous artificial mathematics is commonly used to simulate the observed resonance lineshapes and it has to be shown to give similar results as the correct equations given by Feher and Dyson [45, 47]. Nevertheless, when A/B exceeds 2.6, Dyson’s theory anticipates the presence of diffusive effects, A/B ≳ 2.6 → T_D/T_2 ≪ 1, (figure 7 from [45]) [45, 47]. This means that the resonating spins diffuse across the skin depth with a diffusion time T_D comparable to the spin–spin relaxation time, T_2.

Therefore, following the ideas given above equation (1) gives the derivative of the admixture of absorption (χ″) and dispersion (χ′) of Lorentzian lineshapes,

\[
\frac{d[(1 - \alpha)\chi'' + \alpha\chi']}{dH} \approx \chi_0 H_0 \gamma_0^2 T_2^2 \frac{2(1 - \alpha)x}{(1 + x^2 + s)^2} + \frac{\alpha(1 - x^2 + s)}{(1 + x^2 + s)^2} \frac{x = (H_0 - H)\gamma_0 T_2}{(kOe)}
\]

where H_0 and H are the resonance and the applied magnetic fields, respectively, γ is the gyromagnetic ratio, T_2 is the spin–spin relaxation time, α is the admixture parameter of absorption (α = 0) and dispersion (α = 1), and χ_0 is the paramagnetic contribution from the static susceptibility.

In the following, the analysis of the resonance lineshape also takes into account the saturation term s ≈ γ^2H_0^2T_2 where has been phenomenologically introduced in equation (1). H_1 is the strength of the microwave magnetic field and T_1 is the spin-lattice relaxation time [39].

Figure 2 presents the ESR spectra of Nd^{3+} in Y_{1−x}Nd_xBiPt for x = 0.002 as well as the natural Gd^{3+} impurities at T = 1.6 K, P_{mic} ≈ 5 mW and λ ≈ 132. The inset shows the ESR lineshape for Gd^{3+}.
the very same site in the material. Moreover, except for their
distinct concentrations and Russell–Saunders (L – S) coupling,
both magnetic probes are under the same experimental
conditions, i.e. T, P, and particles size much larger than the
skin depth.

Figure 3(a) shows the ESR spectra of Y1−xNdxBiPt for
x = 0.10 at T = 4.2 K, Pwμ ≈ 8 μW, and 6.6 ≲ λ ≲ 132.
Remarkably, it is clear from these data that the observed change
of the lineshape, going from A/B = 3 for large particles to
A/B ≈ 7 for smaller particles, does not correspond to the
A/B values expected from Dyson’s theory for diffusionless
ESR lineshape (1 ≲ A/B ≲ 2.6). Instead, the lineshape of the
smaller particles presents a strong diffusive shape, A/B
≈ 7 → T0/Γ ≈ 0.2, despite the fact that the particle size is still
larger than the skin depth δ. Figure 3(b), in turn, presents the
Pμ dependence of the ESR lineshape for the 66 ≲ λ ≲ 132
sample. This data show that the ESR lineshape is closer to the
diffusionless limit (A/B ≈ 4 → T0/Γ ≈ 0.9) at very low
power (≈2 μW). However, by increasing Pμ up to ≈ 200 μW
the lineshape becomes completely diffusive (A/B
≈ 14 → T0/Γ ≈ 0.02). Yet, up to this power level the doubly
integrated ESR spectra grow linearly with [Pμ]1/2 showing no
saturation effects (not shown). Again, these results add up to
contrasting behavior displayed by the ESR lineshape of local-
ized magnetic moments in this material. By further increasing
Pμ, the lineshape remains diffusive and the doubly integrated
spectra begin to saturate instead of displaying saturation effects
above ≈5 mW (see figure 6(b) below), confirming the absorption character of the
diffusive resonance lineshape.

Figures 4(a)–(c) display the Pμ dependence of the ESR
lineshape of Y1−xNdxBiPt for x = 0.002, 0.005 and 0.10,
respectively, with 6.6 ≲ λ ≲ 30 at T = 4.2 K. These results
show that our smallest particles present almost diffusion-
less lineshapes (A/B ≈ 2.2 – 2.5 → T0/Γ ≈ 1) at low
concentration (figure 4(a)) and strong diffusive lineshapes
(A/B ≈ 9 – 17 → T0/Γ ≈ 0.10 – 0.01) at high concentration
(figure 4(c)), both nearly independent of Pμ. Nonetheless, the
lineshape presents a dramatic and unusual change between these two regimes for intermediate concentrations, e.g.
X = 0.005 in figure 4(b) (also see figure 3(b)). This sample
shows a diffusionless ESR lineshape (A/B ≈ 2.3 → T0/Γ ≈ 1)
with low Pμ ≈ 3 μW although its lineshape becomes notice-
able more diffusive (A/B ≈ 3.3 → T0/Γ ≈ 0.9) upon increasing Pμ up to an intermediate value of about 80 μW.
Yet, up to these power levels, the ESR spectra do not show
saturation effects (e.g. saturation of ESR intensity). By
further increasing Pμ, the lineshape remains diffusive and the
ESR intensity (doubly integrated spectra) saturates at higher
power levels, similarly to the data presented in figures 6(a)
and (b), confirming again the absorption character of the
diffusive resonance lineshape.

Figures 5(a)–(c) present the T dependence of the ESR
lineshape of Y1−xNdxBiPt with 6.6 ≲ λ ≲ 30 for x = 0.002
at Pμ = 5 mW, x = 0.005 at Pμ = 5 mW and x = 0.10 at
Pμ = 0.2 mW, respectively. These results show that at
T ≈ 10 K the ESR lineshape displays strong diffusive char-
acter. The increase of T tends to restore the ESR lineshape
in the diffusionless regime (A/B ≈ 2–4) as observed at low-Pμ
for large particles (see figures 3(a) and (b)).

Figures 6(a) and (b) display the Pμ and T dependence of the ESR
intensity of Y1−xNdxBiPt with 6.6 ≲ λ ≲ 30 for x = 0.002 and 0.10, respectively. Similar results were obtained
for x = 0.005 and x = 0.05 (not shown). Notice that the reso-
nance intensity for x = 0.10 also saturates above ≈5 mW
in spite of its diffusion-like lineshape; again, confirming the
absorption character of the diffusive resonance lineshape.
We may thus conclude that the ensemble of Nd3+ ions in
Y1−xNdxBiPt (0.002 ≲ x ≲ 0.10) saturates as Pμ increases
and T decreases. Strikingly, regardless of the sample concentra-
tion, the observed saturation effects are a signature of an
insulating character of the system as far as its relaxation pro-
cess is concerned. Figure 6(c) presents the x dependence of the
ESR spectra in Y1−xNdxBiPt (0.002 ≤ x ≤ 0.10) at 4.2 K
and Pμ = 5 mW for 6.6 ≲ λ ≲ 30. The red solid lines are best
fits of the observed spectra to equation (1) using 1/Γ as a
fitting parameter and both H1 and T1 as constant parameters.
The inset to figure 6(c) shows that the linewidth increases
with the Nd$^{3+}$ concentration. This is a typical signature for an inhomogeneous broadening due to Nd$^{3+}$–Nd$^{3+}$ magnetic interaction. Also, since there is no relaxation via the Korringa mechanism (exchange interaction between Nd$^{3+}$ and conduction electrons) in Y$_{1-x}$Nd$_x$BiPt [43] the line broadening is expected to be inhomogeneous. Even in the case of a homogeneous thermal broadening (Korringa relaxation) invariably there is still a residual $T$-independent linewidth that is inhomogeneous and has different origin such as crystalline defects, chemical disorder induced by doping, spin–spin interaction, etc [50].

Note that a diffusive-like character of the lineshape ($A/B \gg 2.6 \rightarrow T_0/T_2 \lesssim 1$) can be obtained, though fortuitously, using equation (1) for $x = \gamma H^2 T_0 T_2 \gg 1$. The fittings obtained

at low concentration (figure 6(c)) may not seem as good as the others presumably due to the contribution of nonlinear terms at medium and high microwave excitation magnetic field that are not adequately taken into account in this model.

Figure 7 shows the $x$ dependence of the spin–lattice relaxation rate $1/T_1$ of Y$_{1-x}$Nd$_x$BiPt with $6.6 \lesssim \lambda \lesssim 30$ at $T = 4.2$ K. The $1/T_1$ values were obtained from the analysis of the saturation factor [51] of the Nd$^{3+}$ ESR intensity. The thick solid line is a guide to the eyes.

### 4. Analysis and discussion

The Dysonian ESR lineshape of diluted Gd$^{3+}$ and Nd$^{3+}$ in YBiPt (figure 2), combined with the change of the Nd$^{3+}$ ESR lineshape with the particle size (figure 3(a)) assure us that these REs are probing the presence of $ce$ within the skin depth $\delta \approx 15 \mu$m. On the other hand, we have already demonstrated that the spin-lattice relaxation via the exchange coupling between the RE localized magnetic moments and $ce$ is very weak in this system. This was the subject of a previous study on crystal field effects of diluted REs (Nd$^{3+}$, Gd$^{3+}$ and Er$^{3+}$)

6 The phonon–bottleneck is characterized by a poor thermal contact between the lattice-phonon reservoir and the thermal bath (Kapitza resistance), confining the energy absorbed at resonance by the local moments to be back and forth, via SO coupling, between the localized magnetic moments and lattice-phonons. As such, higher local moment concentration will lead to stronger confinement.
in Y₁₋ₓREₓBiPt [42, 43]. This conclusion was drawn mainly based on the very small thermal broadening of the ESR linewidth (Korringa relaxation rates) along with the negligible g-shifts (Knight shifts) measured for these REs [43]. These findings were also corroborated by the small Sommerfeld coefficient (\(\gamma < 0.1 \text{ mJ mol}^{-1} \text{ K}^{-2}\)) found in this material [43]. They are all quite consistent with the small gap (\(\Delta \approx 0.1 \sim 0.01 \text{ eV}\)) reported for YBiPt [33, 34, 42, 43].

Thus, the relaxation of localized magnetic moments to the thermal bath should be mainly processed throughout the lattice phonons via their own SO coupling (\(\lambda_{s\text{q}}L_{\text{Nd}} \cdot S_{\text{Nd}}\)) [52] as is the case of any insulator in the diluted limit and not by the exchange interaction with ce \((g_j - 1)J_{\beta\text{Nd}} \cdot s_{\beta}\) as usually occurs in metallic hosts [53].

As such, in spite of the observed metallic (Dysonian-like) ESR lineshapes [45, 47] displayed in figures 3–6, the low-\(T\) ESR linewidth of diluted REs in YBiPt is expected to be inhomogeneous (see figure 6(c)) and the spin–spin relaxation time much shorter than the spin-lattice relaxation time \(T_2 \ll T_1\) as observed for any conventional insulator. Moreover, figures 6(a) and 6(b) show that the Nd\(^{3+}\) ESR intensity saturates for \(T \lesssim 20 \text{ K}\) and \(P_\text{mic} \gtrsim 5 \text{ mW}\), confirming the slow spin-lattice relaxation rate \(1/T_1\). A direct conclusion is that the relaxation process is actually driven by phonons via SO coupling. This result combined with the particle size (figure 3(a)), microwave power (figures 3(b) and 4(a)–(c)), temperature (figures 5(a)–(c) and concentration (figure 6(c))) dependencies of the Nd\(^{3+}\) (I\(\Delta\) Kramers’ doublet; \(S_{\text{Nd}} = 1/2\)) ESR lineshape indubitably assure us that insulating and metallic behaviors coexist within the skin depth \((\delta \approx 15 \mu \text{m})\) of YBiPt.

Now, for the ESR spectral analysis we shall go back to equation (1). It is worth noting that the phenomenological lineshape analysis used here must be taken with caution. In this approach, we incorporated the saturation term \(s = \gamma^2 H_0^2 T_2 T_1\) into the admixture of absorption and dispersion to fully explain the lineshape changes and take into account the spin-lattice relaxation time \(1/T_1\) from the corresponding ESR saturation data. It is possible that this procedure may not capture all details related with the complex phenomenon involving the process of resonant microwave absorption diffusing to the thermal bath in the presence of a phonon-bottleneck process, which is further discussed below.

Figure 8(a) shows the simulations of the data of figures 3(b) and 4(b) using equation (1). The spin–spin, \(1/T_2\), and spin-lattice, \(1/T_1\), relaxation rates were kept constant. The simulated spectra show that the ESR lineshape changes from a diffusionless to a greatly diffusive-like regime as \(P_\text{mic}\) increases. Despite a small broadening, these simulations reproduce the general lineshape features presented in figures 3(b) and 4(b) reasonably well. However, in order to eliminate this extra broadening, which is not observed experimentally, we forced the narrowing of the linewidth \(\Delta H = 1/\gamma T_2\) as \(P_\text{mic}\) increases keeping \(1/T_1\) constant.

The result is presented in figure 8(b) which displays the simulated spectra for the ESR data of figure 4(b). The inset to figure 8(b) shows the extracted phenomenological \(P_\text{mic}\) dependence of \(1/T_2\). Notice that the narrowing of the linewidth begins around \(P_\text{mic} \approx 5 \text{ mW}\) where the resonance starts to saturate (non-thermal equilibrium) (see figures 6(a) and 6(b)). From this point on, an exponential behavior is obtained for the spin–spin relaxation rate, \(1/T_2 \approx \exp(-\alpha P_\text{mic})\), where \(\alpha\) is a fitting parameter. The decrease of \(\Delta H\) with \(P_\text{mic}\) can be ascribed as a reduction of \(1/T_2\) due to an evanescent local fluctuating field (secular and non-secular broadenings) [54] caused by the saturation of the ensemble of the Nd\(^{3+}\) ions.

Nonetheless, we believe that our most important and remarkable experimental result is the dramatic change of the Nd\(^{3+}\) ESR lineshape from a diffusionless \((A/B \approx 2.6; T_0/T_2 \ll 1)\) to a diffusive regime \((A/B \gtrsim 2.6 \rightarrow T_0/T_2 \ll 1)\) observed for \(P_\text{mic} \lesssim 200 \mu\text{W}\) and \(T \lesssim 10 \text{ K}\). This behavior is clearly seen in the size (figure 3(a)), \(P_\text{mic}\) (figures 3(b) and 4(b)) and \(T\) dependence (figures 5(a)–(c)) of the ESR spectra. For the dependence with \(P_\text{mic}\) shown in figure 4(b), the ESR spectra display a drastic lineshape change well below \(\approx 5 \mu\text{W}\), which is the microwave power limit above which saturation effects begin to be observed (figures 6(a) and 6(b)). Besides, this drastic lineshape change is revealed by our simulated spectra only at \(P_\text{mic} \approx 20 \mu\text{W}\) (see figure 8(a)). It occurs below \(\approx 200 \mu\text{W}\) and \(\approx 80 \mu\text{W}\), respectively, for the samples of figures 3(b) and 4(b) (also for the sample with \(x = 0.05\), not shown). Therefore, we conclude that the lineshape change for \(P_\text{mic} \lesssim 200 \mu\text{W}\) is unrelated to the saturation phenomenon.

Hence, the \(\alpha\) parameter (admixture of absorption/dispersion) in equation (1) was phenomenologically adjusted in the limit of low-\(P_\text{mic}\) to fit the data of figure 4(b). The best fits are presented in figure 8(c). The \(P_\text{mic}\) dependence of \(\alpha\) is shown in the inset of figure 8(c). Note that the fits are not quite able

\[\Delta \approx \gamma_0 \cdot h / g_\mu_B \text{ } g = 2.66(4) \text{ (g-value in insulator), indicating no g-shift. [39], p 876.}\]
the regime where absorption is well below the regime where dispersion clearly to 10 K (figures 5(a)) between 1/T1 and 1/T2, 1/μω are variable fitting parameters. The spin-lattice relaxation rate, 1/μω, was obtained from the saturation data of figure 5(a). Their T dependence are shown in the inset. The dashed lines are guides to the eyes.

to reproduce the two lateral wings of the resonance although they do capture the overall observed lineshape changes at the same Pcw (≈100 μW). This Pcw is well below the regime where the saturation effects start to set in (≈5 mW). The inability of the fits to exactly reproduce the experimental spectra may be due to the simplistic phenomenological approach.

Regarding the T-dependent ESR lineshape of figure 5(a), we show in figure 9 the best fits of the spectra to equation (1). T2 and α were taken as variable parameters and T1 was estimated from the saturation factors [51] of figure 6(a). The obtained T dependences of 1/T1 and 1/T2 and α are shown in the inset to figure 9. These results show that both 1/T1 and 1/T2 rates increase as T increases, restoring the diffusionless lineshape and the local fluctuating field as the ensemble of Nd3+ ions reaches its thermal equilibrium (unsaturated state). In other words, the increasing presence of phonons as T is increased restores the thermodynamic equilibrium conditions. At this point, it is worth mentioning that evidence for ce-phonon interaction has also been visualized in the optical properties of Bi-based TIs, where ce-phonon coupling suppresses the surface conducting states as the temperature rises [55].

Now, let us focus on the striking result shown in figure 7: the Nd3+ spin-lattice relaxation rate decreases as the Nd3+ concentration increases. This is an indication that the Nd3+

Figure 10. Illustrative route diagram for the diffusion of the microwave energy absorbed at resonance to the thermal bath (thick solid blue arrows) assisted by the phonon-bottleneck process. The blue dashed arrows indicate weak coupling mechanism.

Diffusion of microwave energy absorbed at resonance assisted by a “phonon bottleneck process”

Figure 9. The red lines represent fittings to equation (1) of the T dependence ESR lineshape for Y0.989Nd0.002BiPt for 6.6 ≤ λ ≤ 30 and Pcw ≈ 5 mW. The spin–spin relaxation rate, 1/μω, and α are variable fitting parameters. α is the admixture parameter of absorption (α = 0) and dispersion (α = 1). The spin-lattice relaxation rate, 1/T1, was obtained from the saturation data of figure 5(a). Their T dependence are shown in the inset. The dashed lines are guides to the eyes.

Regarding the T-dependent ESR lineshape of figure 5(a), we show in figure 9 the best fits of the spectra to equation (1). T2 and α were taken as variable parameters and T1 was estimated from the saturation factors [51] of figure 6(a). The obtained T dependences of 1/T1 and 1/T2 and α are shown in the inset to figure 9. These results show that both 1/T1 and 1/T2 rates increase as T increases, restoring the diffusionless lineshape and the local fluctuating field as the ensemble of Nd3+ ions reaches its thermal equilibrium (unsaturated state). In other words, the increasing presence of phonons as T is increased restores the thermodynamic equilibrium conditions. At this point, it is worth mentioning that evidence for ce-phonon interaction has also been visualized in the optical properties of Bi-based TIs, where ce-phonon coupling suppresses the surface conducting states as the temperature rises [55].

Now, let us focus on the striking result shown in figure 7: the Nd3+ spin-lattice relaxation rate decreases as the Nd3+ concentration increases. This is an indication that the Nd3+

Figure 10. Illustrative route diagram for the diffusion of the microwave energy absorbed at resonance to the thermal bath (thick solid blue arrows) assisted by the phonon-bottleneck process. The blue dashed arrows indicate weak coupling mechanism.

Diffusion of microwave energy absorbed at resonance assisted by a “phonon bottleneck process”

Figure 9. The red lines represent fittings to equation (1) of the T dependence ESR lineshape for Y0.989Nd0.002BiPt for 6.6 ≤ λ ≤ 30 and Pcw ≈ 5 mW. The spin–spin relaxation rate, 1/μω, and α are variable fitting parameters. α is the admixture parameter of absorption (α = 0) and dispersion (α = 1). The spin-lattice relaxation rate, 1/T1, was obtained from the saturation data of figure 5(a). Their T dependence are shown in the inset. The dashed lines are guides to the eyes.
show a diffusionless lineshape for large particles and diffusive for the small ones. As seen, such results can be predicted by adjusting the $\alpha$ parameter in equation (1) as shown in figures 8(c) and 9. Notice though that even for the smallest studied particle size, their dimensions are still several times larger than the skin depth. We believe that the observed lineshape change is related to the surface/volume ratio which is enhanced as the particle size is decreased. This would favor surface distortions which in turn increase the metallic states within the skin depth of this TNSM compound [16, 19, 29–31] and improve the energy transfer process: long lifetime phonons $\rightarrow$ highly mobile $ce$ $\rightarrow$ thermal bath. Hence, smaller particle size tends to improve the diffusion of the microwave energy absorbed at resonance by the Nd$^{3+}$ ions to the thermal bath.

Furthermore, by considering $T_2 \approx 10^{-9}$ s at low power $P_{mic} \approx 0.002$ mW and knowing that $A/B \approx 14 \rightarrow T_D/T_2 \approx 0.02$ at $P_{mic} \approx 0.2$ mW (see figure 3(b)), the diffusion time $T_D \approx 2 \times 10^{-11}$ sec can be estimated for the highly mobile $ce$ within the strong phonon-bottleneck regime.

It is worth discussing the estimated $T_D$ value enlightened by the intrinsic transport parameters of YBiPt. A carrier density of $n \approx 1.7 \times 10^{18}$ cm$^{-2}$ and an electron effective mass $m^* \approx 0.15m_0$ can be obtained from Shubnikov–de Haas measurements at 0.1 K and the $T$ dependence of the amplitude of the oscillations, respectively, assuming a spherical Fermi surface [34]. From the relation $\rho = \frac{m^*e^2nT}{\pi}$ and using the low-$T$ resistivity $\rho \approx 0.7$ m$\Omega$cm [34] we estimate the $ce$ Coulomb-collision mean time $\tau \approx 4.48 \times 10^{-13}$ s. Thus, a mobility of about 5200 cm$^2$/Vs $\tau^{-1}$ which is the order of the Hall mobility [34] can be predicted by considering $\mu = e\tau/m^*$. Hence, from the ratio $T_D/\tau \approx 44$ we estimate that the $ce$ experience one spin-flip scattering after approximately 50 Coulomb-type collisions. Besides, the Fermi velocity $v_F \approx 3 \times 10^5$ m s$^{-1}$ can be also obtained from the mean free path $l = v_F\tau$ with $l = \hbar k_F/\pi m^* \approx 128$ nm and $k_F = \left(3\pi^2n\right)^{1/3} \approx 3.7 \times 10^8$ m$^{-1}$. Therefore, a $ce$ carrying the energy absorbed at resonance by the Nd$^{3+}$ ions may travel a distance of $\delta \approx 6$ $\mu$m before a spin-flip scattering occurs. This length is comparable with the skin depth $\delta \approx 15$ $\mu$m estimated for Y$_{1-x}$Gd$_x$BiPt and, thus, explains the diffusive lineshape observed by the localized Nd$^{3+}$ in our ESR experiments.

It is also worth mentioning that the microwave photons with energy $\hbar \nu/k_B \approx 0.5$ K may promote electrons across subtly gapped Dirac cones near the sample surface. Thus, the density of $ce$ might increase on the surface of the material with increasing microwave power. As a consequence, the surface conductivity would also increase, affecting the skin depth and favoring the diffusion of the microwave energy absorbed at resonance by the Nd$^{3+}$ ions to the thermal bath. This $ce$ activation can only be induced by electric dipolar transitions associated with the electric component of the applied microwave [57]. Nonetheless, this may not be relevant here since the sample is located at the minimum microwave electric field inside the TE$_{102}$ ESR resonator (cavity) used in our ESR experiments.

Additionally, we should report that a similar study has been performed on Y$_{1-x}$Gd$_x$BiPt for $0.01 \lesssim x \lesssim 0.05$. Saturation effects at low $T$ and high microwave power ($P_{mic} \approx 100$ mW) were also observed, but with an inexpressive phonon-bottleneck effect and much less pronounced changes in the lineshape as a function of Gd$^{3+}$ concentration and microwave power when compared with Y$_{1-x}$Nd$_x$BiPt (Nd$^{3+}$: non S-state, $L \neq 0$; $S_{eff} = 1/2$, two-fold ground state multiplet). The relaxation process due to phonons via spin–orbit coupling is expected to be very different for an S-state ion as Gd$^{3+}$ if compared with a non-S ion as Nd$^{3+}$. The resulting Gd$^{3+}$ ESR spectrum consists of seven crystal field unresolved ESR transitions ($S_{eff} = 7/2$) and, therefore, the Gd$^{3+}$ ions are expected to be less susceptible to the phonon-bottleneck relaxation process than in a non-S ion such as Nd$^{3+}$ ($S_{eff} = 1/2$) [52]. The spin-lattice relaxation time throughout seven channels is certainly very different than that of Nd$^{3+}$. We attribute the remarkable difference between the Nd$^{3+}$ and Gd$^{3+}$ lineshapes to a weakly concentration dependent spin-lattice relaxation of Gd$^{3+}$ ions in YBiPt (not shown) indicating that there is no or less pronounced phonon-bottleneck effect in this case. As mentioned above, the phonon-bottleneck process is crucial for the diffusive effect of Nd$^{3+}$. Besides, the Gd$^{3+}$ resonance was obtained under exactly the same experimental conditions of matching, tuning and AFC as for the Nd$_3$ diffusive-like lineshape. Therefore, lineshape distortions due to extrinsic dispersive effects would be very unlikely.

5. Conclusions

The systematic ESR study of the Nd$^{3+}$ $\Gamma_6$ Kramers’ doublet ($S_{eff} = 1/2$) CEF ground state in the cubic non-centrosymmetric half Heusler semiconductor/semimetallic compound Y$_{1-x}$Nd$_x$BiPt revealed that this system presents, simultaneously, metallic and insulating features within the skin depth. This dual character was verified by the saturation effects and relaxation processes observed on the Dysonian (metallic lineshape) of the Nd$^{3+}$ ESR spectra. Also, our phenomenological analysis of the the ESR lineshape suggests that saturation effects do affect the local fluctuation field and contribute to slowing down the effective spin–spin relaxation rate, $1/T_2$, i.e. narrowing down the inhomogeneous ESR linewidth.

Moreover, the dramatic evolution of the lineshape between diffusionless ($A/B \lesssim 2.6 \rightarrow T_D/T_2 \gtrsim 1$) and diffusive regimes ($A/B \gtrsim 2.6 \rightarrow T_D/T_2 \lesssim 1$) in the absence of saturation effects ($P_{mic} \lesssim 200$ $\mu$W), strongly suggests that this peculiar behavior is caused by a subtle combination between the increasing presence of the phonon-bottleneck process (as the Nd$^{3+}$ concentration increases) and the highly mobile $ce$ in this tunable topologically nontrivial semimetal.

In conclusion, the phonon-bottleneck process allowed us to observe the striking diffusive effect on the Nd$^{3+}$ ESR metallic lineshape in YBiPt. We argue that, within the skin depth ($\delta \approx 15$ $\mu$m), the phonon-bottleneck process yields a long lifetime phonon reservoir where the $ce$-phonon SO coupling permits highly mobile $ce$ at the Fermi level, carrying microwave energy absorbed at resonance by the Nd$^{3+}$ ions, diffuses it across the skin depth and, finally, deliver it to the thermal bath.
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