Photoinduced second harmonic generation of LaFe$_4$Sb$_{12}$ near spin fluctuated critical points

K. Nouneh$^{1,3}$, R. Viennois$^{1,4}$, I. V. Kityk$^{2,3}$, F. Terki$^1$, S. Charar$^1$, S. Benet$^1$, and S. Paschen$^4$

$^1$ Groupe d’Etude des Semiconducteurs, CNRS-UMR 5650, Université Montpellier II, Pl. Eugène Bataillon, 34095 Montpellier Cedex 5, France
$^2$ Institute of Biology and Biophysics, Technical University of Czestochowa, Al. Armii Krajowej 36, Czestochowa, Poland
$^3$ Laboratoire de Physique Appliquée et Automatique, Université de Perpignan, Bld. Villeneuve, Perpignan, France
$^4$ Max-Planck-Institut für Chemie fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

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The temperature dependence of the resistivity, the Seebeck coefficient and photoinduced second harmonic generation (PISHG) are studied near the quantum critical point in the skutterudite compound LaFe$_4$Sb$_{12}$, possessing increased spin fluctuations. We observed a large maximum of the PISHG at a temperature of about 15 K. The PISHG signal increases substantially below 35 K. We found a correlation between the temperature dependences of PISHG, resistivity and Seebeck coefficient. We proposed a phenomenological explanation for the occurrence of the PISHG signal in LaFe$_4$Sb$_{12}$ implying strong spin fluctuations exist in this system, which may present some interest for the study of other spin fluctuation systems. Physical insight into the phenomenon observed is grounded in the participation of anharmonic electron–phonon and electron–paramagnon interactions stimulated by inducing light in the interactions with the photoexcited dipole moments.

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1 Introduction

Thermoelectric materials have recently attracted considerable interest because of the current problems of pollution and the appearance of new concepts that have allowed the discovery of promising new thermoelectric materials. Among these, a new group called “filled” skutterudite composites of general formula RM$_4$X$_{12}$ (where R is a rare- or alkaline-earth or actinide element; M = Fe, Ru or Os; X = P, As or Sb) have been subject to specific attention. Rare-earth (RE) atoms are added to two vacancy positions of the conventional unit cell built from the binary compounds (space group $I_\text{m}3$ or $T_d^5$), and that has the effect of decreasing the thermal conductivity of the latter by one order of magnitude [1, 2]. In Fig. 1, the positions of the atoms inside the unit cell are shown.

These compounds have recently attracted much attention because of their extremely large figure of merit $Z = (S^2\sigma/\kappa)$, which is the main requirement for thermoelectric applications [1, 2]. Here $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa = \kappa_e + \kappa_l$ is the thermal conductivity, which includes both the electron and phonon contributions. Besides, these filled ternary compounds exhibit a large variety of electronic properties, where the magnetic behavior is dominated by the particular 4f
electronic configuration of rare-earth elements. Several features like those related to Kondo and heavy-
fermion behavior, various types of magnetic ordering, semiconductivity with a hybridization gap, and
superconductivity have already been revealed [3, 4]. Very recently, the existence of some Pr heavy-
fermion compounds and notably the discovery of the heavy-fermion superconductor PrOs4Sb12 has very
much excited the scientific community [5, 6]. To increase the figure of merit, it is necessary to enhance
the power factor $S^2 \sigma$ (characteristic of strongly doped semiconductors) and to reduce the phonon thermal
conductivity $\kappa$. The study of electron–phonon anharmonic interactions existing in these compounds may
be useful to reduce the thermal conductivity. Recently, among the skutterudite compounds, we have
shown that there is a non-Fermi-liquid behavior in LaFe4Sb12, which originates from the spin fluctuations
associated to the strongly enhanced itinerant paramagnetism observed in this compound [6, 7]. In the
case of spin fluctuations, the energy quanta associated to the excited levels are called paramagnons and
are described by Bose–Einstein statistics [8]. Such statistics is similar to the phonon and it is important
for the understanding of the photoinduced non-linear optical experiments, as we will see below, particu-
larly due to the presence of electron–boson anharmonicity. More details about spin fluctuations and
paramagnons will be developed in the discussion section.

A method of photoinduced second harmonic generation (PISHG) was recently widely used for inves-
tigation of the effective electron–phonon anharmonic interaction during different phase transitions, in-
cluding superconducting, antiferromagnetic, ferromagnetic, etc. [9, 10].

One of the advantages of this method consists in the possibility of performing measurements with mac-
roscopically centrosymmetric materials, where optical SHG is forbidden. At the same time, this method is
particularly effective for determination of the local non-centrosymmetry, which may be caused by electron–
phonon or electron–paramagnon local disturbances due to spin fluctuations in materials like LaFe4Sb12.

Using the PISHG for macroscopically centrosymmetric (randomly disordered) materials is based on
the possibility of photoorientation of the excited-state dipole moments by a polarized photoinducing
beam. The latter, due to interaction with a generally non-centrosymmetric electron–boson subsystem
(like a phonon or paramagnon), results in an output non-zero polarization of the matter existing for the
short (tenths of a picosecond) time of the photoinducing excitation. Generally, under the influence of
powerful light beams, this excited system may be non-centrosymmetric due to superposition of anhar-
monic electron–phonon (or paramagnon) interactions described by a third-rank polar tensor. Particularly
due to excitation of large number of phonons (or paramagnons) through piezoelectric and electrostricted
interactions there appeared an additional possibility to operate by the excited dipole moment sub-system
(see Fig. 2). One can see that the polarized inducing light creates orientation of the excited state dipoles
remaining the ground states unchanged due to mechanical stiffness. So we deal with interactions of the
excited dipole moments which are temporary occupied by photoinduced carriers with phonon and para-
magnon boson subsystems. The latter demonstrate substantial temperature dependence near the phase
transition temperature and critical points. So one can expect that the excited dipole moments of the states
should feel the temperature anomalies near the critical points. Particularly, near the critical points, such
temperature dependences should demonstrate several singular dependences. The PISHG is strongly re-
lated with the excited dipole moments subsystems. So one can expect the occurrence in the correspond-
ing temperature dependences of appropriate anomalies.

Fig. 1 (online colour at: www.pss-b.com) Structure cry-
stellalgraphic of filled skutterudites RM4X12 with the rare-
earth atom R located at the (2a) site situated at the origin
of the unit cell.
Fig. 2 (online colour at: www.pss-b.com) Principal physical mechanism of occurrence the photoinduced non-centrosymmetry.

In the present paper, the PISHG is used as the main tool for studying very weak electron–boson anharmonic interactions enhanced by low-temperature ordering, including spin alignment, and for verifying the origin of the temperature maximum of the PISHG signal in LaFe₄Sb₁₂ observed at low temperature, compared to CeFe₄Sb₁₂ [11].

2 Synthesis of samples

The principle of synthesis is the direct reaction between the elements (Ce: 99.9%; La: 99.9%; Fe: 99.999%; Sb: 99.999%). The details of the specimen synthesis and their “features” were previously reported [11, 12]. No secondary phases were detected by X-ray diffraction, although scanning electron microscopy revealed small amounts of RSb₂ (with R = La, Ce) (polycrystalline Sb-based filled skutterudites [1, 4]). The results of our resistivity measurements were in accordance with those reported by Salas [1, 4]. These elements are heated to 1050 °C in a vertical Pyrox furnace maintained at such a temperature for 48 h before carrying out an abrupt quenching. A second annealing process is performed at 700 °C for 4 days below the peritectic decomposition point of the material but above the decomposition temperature of any possible secondary phase [12].

3 Experimental details

3.1 Transport measurements

Resistivity was measured by the Van der Pauw method [13], and consisted of four ohmic contacts on the material surface. The resistivity measurement was performed also using a standard four-probe method because the sample might be obtained in a bar shape. Indeed, thermo-power measurements between 2 and 400 K were performed using a relaxation method as described in Ref. [14] using PPMS apparatus from “Quantum Design” on a bar-shaped sample (Iff3 sample).

3.2 Non-linear set-up

The photoinducing light beam was generated by a picosecond Nd³⁺: YAG laser (λ = 1330 nm; light power of about 25 kW per pulse with a pulse width duration varying between 0.1 and 10 ns, Fig. 3). The polarizers P1 and P2 were supplied by a specific rotating mechanical equipment for operating by incident light polarization. The incident angle varied within the range of 5–13° with respect to the specimen surface. Such a wide range of angle variation is necessary to find a maximal output PISHG signal. It is necessary to emphasize that the phase matching conditions play a crucial role in the reflected PISHG.
Fig. 3 Principal experimental set-up for the measurement of the PISHG. S: Synchronizer for the power of the lasers; P1 and P2: Glan-Thompson polarizers; specimens – magnetic camera for the specimens; PM: photomultiplier; BC: boxcar; MN: grating monochromator; DL: delay line.

The diameter of the light beam spot varied from 0.85 to 1.24 mm. Depending on surface quality, the light spot diameter changed in order to achieve a maximal output PISHG signal. We have found that the surfaces only change the absolute value of the PISHG but did not affect its spectral dependences. The fluorescence spectra lie in the near-UV range (below 380 nm) and we separated this parasitic background from the output PISHG using a grating monochromator.

Because the maximal absorption value of both laser wavelengths is around $10^6 \text{ cm}^{-1}$, one can estimate that the effective thickness of light penetration should be around 6–12 nm. So, we suggest that we rather deal with structural changes near the surface. However, surface states (up to 15 nm) are sensitive to different spin fluctuations appearing in the bulk, so we can expect a manifestation of the bulk properties.

The sample’s temperature was monitored by a microthermometer chip with an accuracy up to 0.2 K. This was done simultaneously from both sides of the samples. The highest observed local heating due to power absorption did not exceed 0.8 K. We obtained previously almost the same value for different investigated metals and superconductors [5, 6].

Moreover, the set-up allows scanning through the specimen’s surface by the beam. The beam profile sequence had a Gaussian-like shape with a dispersion half-width of about 78%. The laser power stability was no worse than 0.1%. The generation of the photoinducing Nd$^{3+}$:YAG laser was temporarily synchronized with that of the Eu$^{3+}$:YAB laser ($\lambda = 1530 \text{ nm}$). This laser beam (spot diameter 0.2–13.6 mm; laser power 6–14 MW; pulse duration 1.3–8.5 ps) was used as a fundamental one for the PISHG. The pulse repetition time was synchronized in time for the photoinducing and probing (fundamental) laser beams. In order to determine light polarization of the photoinducing and probing beams, we have used polarizers with a polarization degree of about 99.998(7)% in the considered spectral range. An electrooptically operated delay line (consisting of an Li$_2$B$_4$O$_7$ single crystal) was used for operation of the pump–probe delay time. It allows us to vary the pump–probe delay time with a time resolution no worse than 0.56 ps. In the result, a mismatch between the laser beams should be corrected. The measurements were done at more than 80 points to achieve reliable statistical averaging by means of a $\chi^2$ distribution with an accuracy smaller than 0.02. The photodetection was carried out by a high-resolution digital photomultiplier (PM) connected to an electronic boxcar integrator and gate of about 650 ps. The grating monochromator (MN) (spectral resolution of about 8.2 nm/mm) was used to separate the doubled frequency signal ($\lambda = 0.765 \mu\text{m}$) from the fundamental Eu$^{3+}$:YAB laser beam ($\lambda = 1.53 \mu\text{m}$). The pumping as well as fundamental signals were monitored by a beam splitter (BS) connected to a synchronized photomultiplier (PM). The absolute value of the output PISHG signal was equal to about $10^{-5}$ times the incident beam power. The maximal output PISHG signal was observed only for the parallel polarization of the photoinducing and fundamental laser beams. When the non-collinearity was higher than 7°, the output PISHG drastically vanished (at least by two orders of magnitude). The non-homogeneity of the output PISHG signal space distribution through the specimen surface was about 6%. From the obtained PISHG dependences, second-order susceptibility values were determined.

The available precision of the PISHG measurements allowed us to determine the output PISHG signal with a relative error less than 0.8%. Therefore, the observed enhancement of the output PISHG signal (up to 7%) was absolutely reliable.
4 Results

4.1 Resistivity and its temperature derivatives near critical points

The study of the thermal variation of the electrical resistivity requires determination of the scattering processes of electrons (by phonons, paramagnons or structural defects) for a better understanding of the whole physical mechanism occurring in LaFe$_4$Sb$_{12}$ and notably for understanding the different results obtained by PISHG.

The thermal variation of the resistivity for two different samples is shown in Fig. 4. This variation seems to be in rather good agreement with that found by Bauer et al. [15]. As we can see in Fig. 5, the resistivity follows the law \( \rho = \rho_0 + A_nT^n \), with \( n = 1.7 \) in both samples. The typical behavior of the Fermi-liquid (FL) feature which corresponds to \( n = 2 \) transformed into a non-Fermi-liquid (NFL) feature. So we believe that the observed phenomena can be associated with a spin fluctuation (paramagnon), resulting from the magnetic instability of a system close to a ferromagnetic quantum critical point (QCP) [14], where the Curie temperature is exactly equal to 0 K. Indeed, in the same temperature range a NFL behavior is also observed in the magnetic susceptibility [6, 7]. The presence of the spin fluctuations in this compound is also confirmed by the field dependence of the magnetization and the heat capacity observed in this temperature range [6, 7].

At high temperature, the temperature variation of the resistivity \( \rho(T) \) is less than linear with \( T \) and is even saturated at higher temperatures in both samples (see Fig. 4). The temperature range for which we
observe this behavior corresponds roughly to the same temperature range where the magnetic susceptibility \( \chi(T) \) follows the Curie–Weiss law [6, 7]. This behavior is in agreement with that predicted by the theoretical model of Coqblin et al. for the spin fluctuations [8].

In the inset of Fig. 4, the resistivity derivative versus temperature for 1 fs3 sample of LaFe\(_4\)Sb\(_{12}\) are reported to show a maximum at about \( T'_{\text{max}} = 55–60 \) K. Sample 1 fs1 exhibits a similar maximum at \( T'_{\text{max}} = 68(\pm 5) \) K, but this maximum is less well resolved than for the 1 fs3 sample (this curve is not shown in the inset of Fig. 4 for better clarity of the figure). This maximum in \( d\rho/dT \) should correspond to the low-temperature limit of the high-temperature regime in \( \rho(T) \) as discussed in the previous section and therefore should be essentially due to the spin fluctuations.

As we have seen in the Introduction, LaFe\(_4\)Sb\(_{12}\) is a kind of NFL compound showing a magnetic instability due to the presence of a paramagnetic transition with strong fluctuations of delocalized spins probably induced by its initial ferromagnetic configuration [6, 7]. This mechanism works only at low temperatures (\( T < 20 \) K) and low magnetic field (\( H < 5 \) T). Indeed, NMR measurements at high field (around 6 T) on the core of La [16] indicate that there are additional antiferromagnetic spin fluctuations in this compound and that the ferromagnetic spin fluctuations should be quenched by the magnetic field. NMR experiments [16] also give other very important information: the La site does not exhibit a strict cubic symmetry but a slightly distorted one, which confirms the non-centrosymmetric configuration of LaFe\(_4\)Sb\(_{12}\).

### 4.2 Seebeck coefficient

The temperature dependence of the Seebeck coefficient \( S \) is shown in Fig. 6. In the inset, below 11–12 K a linear variation of \( T \) is observed with a large slope (here, about \(-0.865 \) \( \mu \)V/K\(^2\)), as often observed in heavy-fermion systems. From Fig. 6, it was found that LaFe\(_4\)Sb\(_{12}\) has an \( S \) minimum at about 40 K, with negative values at low temperatures, while the sign of the Seebeck coefficient becomes positive with increasing temperature. The great change of the Seebeck coefficient in the sign observed at low temperatures is in agreement with the typical magnetic instability reported above for this material due to the proximity of the QCP and is related to the presence of spin fluctuations in LaFe\(_4\)Sb\(_{12}\) [2].

Indeed, similar behavior has been experimentally observed in some other systems with spin fluctuations [8, 17, 18]. From the theoretical point of view [8, 18, 19], there exist two different possible mechanisms (diffusion and paramagnon drag mechanisms) which can explain in equal manner the observed behavior of the thermo-power. From our experimental results, it is not possible to distinguish which is the dominant mechanism. However, for understanding the physical insight of the PISHG signal, it is not important to know which is the prevailing mechanism, because both mechanisms imply spin fluctuations, which are at the origin of the PISHG signal as we will see below.

![Fig. 6 Temperature dependence of the Seebeck coefficient for the 1 fs3 sample of LaFe\(_4\)Sb\(_{12}\). Inset: temperature dependence of the Seebeck coefficient for the 1 fs3 sample at very low temperature (below 11–12 K), showing a linear variation with \( T \).](image-url)
4.3 Photoinduced second harmonic generation

In the Introduction we have mentioned a principle of detection of the spin fluctuation using local non-centrosymmetry introduced by the PISHG which is determined by the local hyperpolarizabilities. Non-linear optics informs on the photoexcited polarized quantum levels which are extremely sensitive to weak long-range non-centrosymmetry interactions.

Generally the polarizability of the medium possess two terms: linear and non-linear [26]:

\[
\alpha_{ij} = \alpha_{ij}^{(0)} + \beta_{ijk}^{(1)} + \gamma_{ijkl}^{(2)} E_i E_j E_k E_l, \\
\beta_{ijk}^{(1)} = \beta_{ijk}^{(0)} + \gamma_{ijkl}^{(1)} E_i E_j E_k E_l, \\
\gamma_{ijkl}^{(2)} = \gamma_{ijkl}^{(0)} + \beta_{ijk}^{(2)} E_i E_j E_k E_l.
\]

Here \(\alpha_{ij}, \beta_{ijk}, \gamma_{ijkl}\) are microscopic susceptibilities, which are related to the macroscopic susceptibility by the equations:

\[
\chi^{(1)}_{ij} = L^{(o)}_{ij} \alpha_{ij}, \\
\chi^{(2)}_{ij} = L^{(o)}_{ij} L^{(o)}_{kl} \beta_{ijk}, \\
\chi^{(3)}_{ijkl} = L^{(o)}_{ij} L^{(o)}_{kl} L^{(o)}_{mn} \gamma_{ijkl}.
\]

where the \(i, j, k\) correspond to crystallographic components of the crystals, \(\rho\) is the density of the medium, and \(\chi^{(o)}\) is the macroscopic second-order non-linear susceptibility responsible for the PISHG.

Using the oversimplified expression we can present the microscopic hyperpolarizability within a framework of a two- and three-level model:

\[
\alpha_{ij} \approx \frac{\mu_i \mu_j}{E_s^2}, \\
\beta_{ijk} \approx \frac{\mu_i \mu_j \delta \mu_k}{E_s^4}, \\
\gamma_{ijkl} \approx \frac{\mu_i \mu_j \mu_k \mu_l}{E_s^4}.
\]

Here \(\mu_i\) are transition dipole moments and \(\delta \mu_{ij} = \mu_{ij}^{(e)} - \mu_{ij}^{(g)}\) are differences between excited and ground dipole moments. For measurements of PISHG, the only important parameters for the coefficient \(\beta_{ijk}\) are the excited optically aligned dipole moments. The latter are sensitive to the long-range phonon or paramagnon temperature dependences and give the observed temperature dependences in the macroscopic susceptibility.

Simultaneously it is well known that the conductivity of free electrons may be described as

\[
\sigma = \frac{ne \bar{V}}{\bar{T}},
\]

where \(\bar{T} = \frac{\tau \bar{V}}{}\) is the free path length, \(\bar{V} = \frac{\sqrt{3 k_T m}}{m}\) is the average velocity, and \(n\) is the electron density.

The dipole moment may be expressed as

\[
le = \mu, \\
\sigma = \frac{ne \bar{V}}{\sqrt{3 m k_T}} \mu.
\]
The dipole moment has two contributions, \( \mu = \mu_{\text{el}} + \mu_{\text{ph}} \), where \( \mu_{\text{el}} \) is the dipole moment’s electronic part, which is less dependent on temperature, and \( \mu_{\text{ph}} \) is the dipole moment’s phonon part, which is more dependent on the temperature as bosons are sensitive to anharmonic electron–phonon (paramagnon) interactions. The latter term is described by third-order derivatives of the anharmonic potential

\[
\gamma_{ijk} = \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k},
\]

or

\[
U = \frac{1}{2!} \alpha_{ij} x^i x^j + \frac{1}{3!} \beta_{ijk} x^i x^j x^k + \frac{1}{4!} \gamma_{ijkl} x^i x^j x^k x^l.
\]  

(9)

This anharmonic interaction gives an additional contribution near the critical points, which is described by the expression:

\[
\mu_{\text{ph}} \approx \frac{\gamma_{ijk}}{(T - T_c)^2}
\]

(10)

where \( T_c \) corresponds to the phase transition (critical) temperature in the case of superconducting, magnetically ordered compounds, etc. [9, 10]. In the case of spin fluctuations system, \( T_c \) corresponds to the characteristic temperature of the spin system, i.e. to the spin fluctuation temperature \( T_{sf} \). This additional contribution to the anharmonic potential may explain the observed temperature dependence of the output optically induced susceptibility if it is due to the spin fluctuations, as we will discuss in more detail in the next section.

In Fig. 7 is reported the temperature dependence of the PISHG signal for the lfs3 sample of LaFe\(_4\)Sb\(_{12}\). We can see that the signal appears below 35 K and reaches a maximum around 15 K. Also, the PISHG signal shows a decrease of the pump–probe delay time in the PISHG with temperature (Fig. 8). Contrary to the other skutterudite compounds [8], the shape of the temperature-dependent maxima is almost unchanged. So we have only a temperature shift, which indicates the crucial role of spin fluctuations in the observed temperature dependences as well in the pump–probe relaxation kinetics.

Indeed, when \( T \) increases and \( T \geq T_{sf} \), the lifetime (\( \tau = \hbar / \Delta \omega \)) of the spin fluctuation and the corresponding excitations (paramagnon) decreases rapidly when one is far from the ferromagnetic instability. As a result, the peak of the PISHG decreases rapidly and disappears at very high temperature, as experimentally observed in Figs. 7 and 8.

![Fig. 7](image-url)
The delay time values are typical for the anharmonic electron–phonon relaxation times. So one can expect that the observed dependences confirm the principal role of the electron–phonon interactions in the observed phenomena.

4 Discussion

First, we wish to show that we can explain the appearance of the strong PISHG by the presence of spin fluctuations in LaFe$_4$Sb$_{12}$, particularly near the critical points. As we have seen in the previous section, there are some conditions for obtaining a PISHG signal. We should have non-centrosymmetry in the crystallographic structure. As the NMR experiments [16] suggest, that is the case in our compound due to the distortion of the cubic symmetry in the La site and the occurrence of slight non-centrosymmetry. We should have a strong singularity in the spectrum of the boson system which interacts effectively with the electron subsystems and particularly excited dipole moments. Usually, in the materials previously studied by the PISHG experiments this boson system was the phonon system, as was notably the case for high-$T_c$ superconductors. However, one cannot exclude completely a possible role of the antiferromagnetic domains. There exist also some other cases (for magnetically ordered compounds) for which the boson system was constituted by the energy quanta of the spin waves, called magnons. Here, we are in a close but different case than the latter one. Indeed, in the strongly enhanced paramagnetic compounds (i.e. paramagnetic compounds close to the QCP), there exist only damped spin waves, also called spin fluctuations [8]; whereas in the magnetically ordered systems, there exist at the same time “true” spin waves (at low $Q$ wave vector) and damped spin waves [8] (at higher $Q$). The energy quanta of the latter are called paramagnons [8]. Thus, in compounds such as LaFe$_4$Sb$_{12}$, which is still paramagnetic but close to the QCP, there are increased spin fluctuations [6, 7, 20]. These latter ones give us the boson distribution for which the bosons correspond to the paramagnons. Now, we have shown that the paramagnons form the boson distribution which we need, but this is not sufficient to explain the big observed PISHG signal. Indeed, as we have explained in the previous section, we need a singularity in the boson distribution. However, such a singularity exists in the spectral density of the spin fluctuations for low enough temperatures (typically for $T < T_d$), as shown by Coqblin [8] and by Kaiser [21]. However, when the temperature approaches the spin fluctuation temperature $T_d$ (which is typical of the spin system), this singularity tends to decrease and then disappears completely for temperatures high enough compared to $T_d$ (see Ref. [8]). Therefore, this temperature dependence can explain in a natural manner the disappearance of the PISHG signal for temperatures close to $T_d$ (which will be estimated below). Thus, near the critical points we deal with singularities coming from the spin fluctuations.

Because spin–electron as well as electron–phonon interactions will effectively modulate the excited dipole subsystem, one can expect a particular contribution of the anharmonic part, because it is described by third-rank polar tensors and is sensitive to temperature near the critical points and simultaneously due
respectively and the temperature dependence of the transport coefficient seems to exist. Indeed, we can point out that the temperature should be slightly shifted compared to singularity temperature positions of the transport coefficients. But we can also remark that the position of the maximum of the PISHG signal is close to the beginning of the NFL behavior in the resistivity and situated at slightly higher temperature than the beginning of the linear behavior of the Seebeck coefficient \(S(T)\) (below 10–12 K), but we have no real theoretical support for explaining this. On the other hand, we also should note that \(T_{\text{min}}\) of the same order of magnitude as \(T_{\text{max}}\) which is often used for estimating \(T_{\text{sf}}\) [8, 21]. But, in both cases, we only obtain a good order of magnitude for the value of \(T_{\text{sf}}\). Therefore, because \(T_{\text{PISHG}}\) has the same order of magnitude as \(T_{\text{sf}}\) defined in the manner as explained above, we propose that maybe we could also use \(T_{\text{PISHG}}\) for determining \(T_{\text{sf}}\) in spin fluctuation systems.

Consequently, we propose that the PISHG method may be a new non-destructive method to detect long-range spin fluctuations in different spin subsystems and for determining \(T_{\text{sf}}\) in such systems. The spin fluctuations are limited for the case of the non-linear optical susceptibility compared to other transport properties since the latter are averaged over all the virtual states [9, 10]. The carrier distribution is hereby a mixture of conduction electrons and anharmonic bosons (paramagnons) leading to the appearance of photoexcited non-centrosymmetry near the critical points.

So far, we have only talked about to the hypothesis of the presence of spin fluctuations for explaining the strong PISHG signal observed in our present experiments. Another possible explanation could be the presence of a localized mode due to the rattling of the rare-earth inside an oversized cage. Such a mode could introduce a singularity in the phonon distribution. However, if this hypothesis were true, we should find almost the same result for the PISHG signal in \(\text{LaFe}_4\text{Sb}_{12}\) as in \(\text{CeFe}_4\text{Sb}_{12}\), which is not the case. Indeed, the PISHG signal is much higher in the \(\text{La}\) than in the \(\text{Ce}\) compound [11].

Now, we wish to compare the non-linear optical properties of both compounds with their heat capacity \(C_p\). In Refs. [4, 6, 15, 22], the Sommerfeld coefficient \(\delta\) (for convenience of notation, because we have already used this symbol in presenting the theoretical non-linear photoinduced optical model, we use \(\delta\) and \(\delta_{\text{sf}}\) for respectively the Sommerfeld coefficient and the phonon part of the heat capacity instead of respectively \(\gamma\) and \(\beta\) in the usual notation) of both compounds has been determined by extrapolation of \(C_p/T\) vs. \(T^2\) at \(H = 0\) T for \(T > 2\) K by the equation

\[
C_p/T = \delta + \beta T^2.
\]  

(11)

The electronic specific heat \(\delta\) is three times larger for \(\text{LaFe}_4\text{Sb}_{12}\) [6, 15] than for \(\text{CeFe}_4\text{Sb}_{12}\) [4, 22] \((\delta = 195\ \text{mJ/mol K}^2\) and \(\delta = 60\ \text{mJ/mol K}^2\), respectively) and than the value calculated from band-structure calculations. Thus, it is interesting to see if we can find a common explanation for these last results with the ones of the PISHG experiments. Before doing that, we should remind the reader that \(\text{Ce}\) is trivalent in this last compound [12], permitting a direct comparison between both compounds.

For analyzing the heat capacity results, we consider that \(\delta\) consists of two terms: \(\delta = \delta_{\text{e}} + \delta_{\text{sf}}\), where \(\delta_{\text{e}} = (\pi/3)^2k_B^2N(E_F)\) \((N(E_F)\) is the electronic densities of states) is the electronic contribution, which can be calculated from band-structure calculations, and \(\delta_{\text{sf}}\) is the contribution of the spin fluctuations [6, 23].
A first hypothesis for explaining both the larger $\delta$ and PISHG signal in LaFe$_4$Sb$_{12}$ is to assume an increase of $\delta E$ and therefore of $N(E_F)$ in the La compound compared to the Ce one. Indeed, if the substitution of cerium by lanthanum modifies the cell parameters a little and the localization and shape of the iron 3d band remain almost unchanged, the position of $E_F$ in the iron 3d band and therefore $N(E_F)$ are not the same in the Ce and La compounds. In the case of the La compound, the position of $E_F$ is localized closer to the maximum of the iron derived density of states than for the Ce compound and thus $N(E_F)$ and $\delta$ are larger in the La than in the Ce compound [24]. In the case of this hypothesis, the second-order optical susceptibility determined by microscopic hyperpolarizability (see Eqs. (3)–(6)) reflects the contribution of the electron charge density through the non-centrosymmetry carrier distribution. So in this case due to superposition of the polarized photoinducing beam one can expect the occurrence of a photoexcited state dipole subsystem effectively modulated by the photoexcited boson (phonon or paramagnon, here) subsystem described by third-rank polar tensors. Near the critical temperature determining the singularity in the corresponding susceptibilities (which is related to the spectral density of the paramagnons) there occurs the observed increased PISHG in the La compound. The 4f level of the La atom is strongly localized and non-magnetic because its 4f term is empty. The conduction electrons interact with the Fe 3d level and Sb 5p level, Fe is sensitively less localized and, hence, it should manifest an itinerant magnetism, so the photoinduced effects are mainly caused by delocalized states of Sb 5p which are coordinated with Fe 3d states.

A second hypothesis for explaining the larger $\delta$ in LaFe$_4$Sb$_{12}$ than in CeFe$_4$Sb$_{12}$ is the presence of a large $\delta E$ contribution in LaFe$_4$Sb$_{12}$, which is almost absent in CeFe$_4$Sb$_{12}$. This large $\delta E$ contribution should be the main reason why $\delta$ is much larger for the La compound than for the Ce one and for the one predicted by band-structure calculations. This last observation strongly supports this second hypothesis, which is also the natural explanation of the large observed PISHG signal in LaFe$_4$Sb$_{12}$, as stated previously in the first part of the discussion. Therefore, in our opinion, the hypothesis of the presence of strong spin fluctuations in LaFe$_4$Sb$_{12}$ is the better and the more natural one for easily explaining at the same time the stronger PISHG signal and the larger Sommerfeld coefficient $\delta$ observed in LaFe$_4$Sb$_{12}$ than in CeFe$_4$Sb$_{12}$.

Finally, we wish to remark that if we can explain why we observe a large signal of the PISHG in LaFe$_4$Sb$_{12}$, we still have some difficulties understanding the origin of the small signal of PISHG in CeFe$_4$Sb$_{12}$ [11] and why it is so small. Indeed, this compound presents a Kondo effect with a rather elevated Kondo temperature ($T_K \approx 80$ K) [7, 22, 25] and we could expect that the Kondo spin fluctuations should also give a big PISHG signal as in the case of the La compound. The only tentative explanation that we can actually propose is that the PISHG experiments are more sensitive to spin fluctuations due to itinerant paramagnetism than to spin fluctuations coming from the Kondo effect and/or the localized magnetism.

### 5 Conclusion

We have found experimentally an increase of the PISHG in the vicinity of the low-temperature critical point in enhanced paramagnetic material LaFe$_4$Sb$_{12}$ possessing strong spin fluctuations. Comparison with temperature behaviors of transport and thermoelectric properties indicates a crucial role of singularities in the corresponding temperature dependences of electron–paramagnon interactions. This is confirmed by pump–probe relaxation of PISHG as well as by general phenomenological considerations. Physical insight into the phenomenon observed is grounded in the participation of anharmonic electron–phonon and electron–paramagnon interactions stimulated by inducing light in the interactions with the photoexcited dipole moments.

Consequently, we can propose that the PISHG method may be a new non-destructive method to detect long-range spin fluctuation in different spin subsystems and for determining the spin fluctuation temperature $T_{sf}$ in such systems.

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References

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