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Low-temperature anomalies of photoinduced second harmonic generation in skutterudites

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Abstract

Photoinduced second harmonic generation (PISHG) was found in skutterudite compounds of $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$. Measurements versus temperature, pump–probe delaying time and external magnetic field were performed. The studied compounds belong to moderate heavy fermion compounds (HFC) in the ground state. The PISHG signals appear at 6.8 and 4.9 K for $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$, respectively. We suspect that these signals are due to anharmonic electron–phonon interactions creating a charge density non-centrosymmetry. The observed effects are caused either by a possible phase transition or by drastic changes in the electron structure of the HFC with decreasing temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Compounds with a skutterudite structure (space group $Im\bar{3}$ or T_h^5) have recently attracted much attention due to their promising thermoelectric properties [1, 2]. Among these materials, the binary compounds have relatively large thermal conductivity. Rare-earth (RE) atoms are usually inserted into two vacancies of a conventional unit-cell of these binary compounds to decrease their thermal conductivity, and ‘filled’ skutterudites with unit-formula RM_4X_{12} (where R is the rare- or alkaline-earth or actinide; M = Fe, Ru or Os; X = P, As or Sb) are obtained. These R atoms are weakly bound in the irregular dodecahedral cluster of X atoms and as a consequence they scatter phonons [2]. Another consequence of the R atom insertion is a remarkable increase in electron concentration compared with semiconducting binary skutterudites. Therefore, this should favour the electron–phonon interaction that is also

responsible for the very low thermal conductivity in $\text{CeFe}_4\text{Sb}_{12}$ compared with $\text{CeFe}_4\text{As}_{12}$ where the electron concentration is lower [3, 4].

Consequently, an understanding of the electron–phonon interaction in the filled skutterudites would be useful in order to optimise their thermoelectric properties. Moreover, the filled skutterudites show a rich variety of electron properties, such as superconductivity ($\text{LaFe}_4\text{P}_{12}$, $\text{LaRu}_4\text{Sb}_{12}$), magnetic order ($\text{EuFe}_4\text{Sb}_{12}$, $\text{NdRu}_4\text{Sb}_{12}$), semiconductivity with a hybridisation gap ($\text{CeFe}_4\text{P}_{12}$, $\text{UFe}_4\text{P}_{12}$) and heavy fermion behaviour ($\text{CeFe}_4\text{Sb}_{12}$, $\text{CeRu}_4\text{Sb}_{12}$) [5–8]. In the last case, the heavy fermion compounds (HFC) may change the electron–phonon interaction in Ce-based systems at low temperatures because of the strong correlation of electrons observed in these compounds [1, 6, 8].

A method of photoinduced second harmonic generation (PISHG) was recently proposed in order to investigate the effective electron–phonon anharmonic interaction during different phase transitions [9–12]. In present paper the PISHG was used as an important tool to study very weak electron–phonon interactions, enhanced by low-temperature ordering. In this way, the enhancement of the electron–phonon interactions could be detected earlier (at temperatures higher than the critical temperature T_c). The skutterudites are materials having low-temperature phase transitions of different kinds due to the presence of transition metal and RE atoms. We will apply the PISHG to detect the electron–phonon interactions before (i.e. at higher temperatures) the appearance of the low temperature phase transformations. The sensitivity of the PISHG is substantially higher than the traditional structural methods [9–12] because it is sensitive to local rearrangement unlike x-ray diffractometry. Because of this, and the important effect of the electron–phonon interaction on the thermoelectric properties of $\text{CeFe}_4\text{Sb}_{12}$, we have investigated $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ by means of the PISHG.

To the best of our knowledge, this is the first study of this class of compound (i.e. the HFC class) by the PISHG technique. It should be emphasised that the PISHG experimental technique has shown its efficiency for the study of the anharmonic electron–phonon interaction in different kinds of phase transformations. The non-local non-centrosymmetry, reflecting the anharmonic electron–phonon interaction, usually appears at higher temperatures than the critical temperature of the superconducting phase, detected using traditional resistivity or magnetic measurements [9–11]. Thus, the appearance of the phase transition should be associated with the anharmonic electron–phonon interaction through different magneto- and electrostriction effects [9–12]. Therefore, the PISHG signal can be observed above the critical temperature. In the same manner, it is possible to detect changes of the electronic structure in the HFC by means of the PISHG experiments.

2. Experimental details

The details of the specimen synthesis and its features were reported previously [13]. No secondary phases were detected by x-ray diffraction, although scanning electron microscope techniques revealed small amounts of RSb_2 (with $\text{R} = \text{La}, \text{Ce}$) (like the ‘start of the art’ polycrystalline Sb-based filled skutterudites [1–8]). Our resistivity measurements were in accordance with measurements by Sales and co-workers [1, 8, 14].

The photoinducing light beam was generated by a picosecond nitrogen laser ($\lambda = 377 \text{ nm}$; light power of about 25 kW with a pulse width duration varying between 4 and 9.8 ps). The principal set-up is presented in figure 1. The value of the pulse duration was defined by the need to avoid specimen overheating. Rotating Fresnel prisms P1 and P2 were supported by special rotating mechanical equipment for operation by incident light polarisation. The incident angle with respect to the specimen surface was varied within the range 5° – 13° . Such a wide range for the angle variation is necessary to achieve a maximal output PISHG signal. We will show

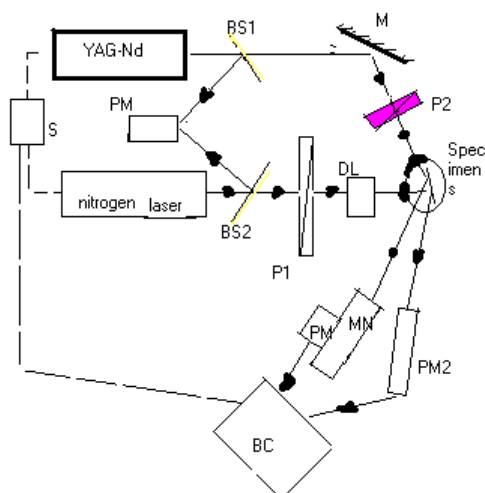


Figure 1. Principal experimental set-up for the measurement of the PISHG. S—synchroniser for the power of the lasers; BS1 and BS2—quartz beamsplitters; P1, P2—Glan Thompson polarizers; Specimens—magnetic camera for the specimens; PM and PM2—photomultipliers; BC—boxcar; MN—grating monochromator; DL—delaying line.

below that phase synchronism conditions play a crucial role in this case. The diameter of the light beam spot was varied from 0.85 to 1.24 mm. Depending on surface quality, the light spot diameter was varied to achieve the maximal output PISHG signal. We have found that the surfaces change only the absolute value of the PISHG and did not influence its spectral dependencies. The fluorescence spectra lie in the near UV range, and we have separated this parasitic background from the output PISHG using a monochromator (MN).

Because the maximum value of the absorption for both laser wavelengths is around 10^6 cm^{-1} one can calculate that the effective thickness of light penetration is around 6–8 nm. So one can suggest that we are dealing with structural changes at the surfaces and the role of the bulk effects is in this case limited.

The sample's temperature was monitored by a microthermobolometer chip with precision up to 0.2 K. The monitoring was done simultaneously from both sides of the samples. The maximum observed local heating due to power absorption heating did not exceed 0.8 K. It was almost the same as that obtained by us earlier during investigations into different metals and superconductors [9–12].

The set-up also allows scanning by the beam through the surface of the samples. The profile sequence of the beam had a Gaussian-like shape with dispersion half-width of about 78%. Stability of the laser power was no worse than 0.1%. Generation of the photoinducing nitrogen laser was temporarily synchronised with generation of the fundamental Nd:YAG laser. An unfocused Nd:YAG ($\lambda = 1.06 \mu\text{m}$) 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 beam for the PISHG. Time repetition of the pulses was synchronised for the photoinducing and probing (fundamental) laser beams up to 0.68 ps. In order to determine the light polarisation of the photoinducing and probing beams, we have used Glan–Thompson polarizers with polarisation degree about 99.998(7)% in the spectral range being considered. An electrooptically operated delaying line (DL) consisting of a $\text{Li}_2\text{B}_4\text{O}_7$ single crystal was used for operation by the pump–probe delaying time. This allowed us to vary the pump–probe delaying time with time resolution no worse than 0.56 ps. As a result, a mismatch between the laser beams could be corrected. For each

specimen the measurements were taken at more than 80 points to achieve reliable statistical averaging using a χ^2 distribution with precision less than 0.02. Photodetection was carried out by digital high-resolution photomultipliers (PM) RCA-121 and FE-124-H combined with an electronic boxcar integrator and gate of about 480 ps. The grating MN SPM-3 (spectral resolution of about 7 nm mm^{-1}) was used to separate the green double frequency signal ($\lambda = 0.53 \mu\text{m}$) from the fundamental Nd:YAG laser beam $\lambda = 1.06 \mu\text{m}$). The pumping as well as fundamental signals were monitored, with the help of the beam-splitters (BS), by the connected synchronised PM. The absolute value of the output PISHG signal was about 10^{-5} times the incident beam power. The maximum output PISHG signal was observed only for the parallel polarisation of the photoinducing and fundamental laser beams. When the non-collinearity was higher than 7° , the output PISHG drastically reduced (by at least two orders of magnitude). The non-homogeneity of the output PISHG signal space distribution through the specimen surface was of about 6%.

The available precision of the PISHG measurements permitted 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%) is absolutely reliable.

3. Results and discussion

All the traditional structural methods (x-ray, EXAFS etc), are sensitive to structural rearrangement during phase transformations. However, based on simple considerations, one can expect a substantial contribution from the electron–phonon interaction. In this case, the precision of the methods above is limited. In our previous papers [9–12], it was shown that the optical PISHG method is more sensitive for observation of such rearrangements of phase transitions than the traditional ones. In fact, this method is also sensitive to the electron charge density non-centrosymmetry caused by the strong electron–phonon interaction.

The photoinducing beam generates free electron carriers as well as electrostricted phonons effectively contributing to the output optical response function through creation of the anharmonic non-centrosymmetric charge density distribution [9–12].

Successive polishing of the surfaces and repeating the PISHG measurements have been done to eliminate surface contributions. We have shown that after polishing of the near-the-surface layer (up to the 0.1 mm) we have observed almost the same PISHG dependencies. Several discrepancies in the absolute values (up to 1.3%) reflect primarily differences in the surface polishing technological process.

In figure 2, the measured temperature dependencies of the PISHG signal for $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ specimens are presented. Features of the obtained dependencies are qualitatively similar. One can clearly see the PISHG signal increasing with decreasing temperature. Such behaviour is typical for spin glasses approaching the critical point [10]. The PISHG signal appears at 4.9 and 6.8 K for $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$, respectively. In order to understand the origin of the observed PISHG signal, we have performed pump–probe delaying PISHG measurements.

It is seen in figure 3 that the maximum PISHG is achieved at a pump–probe delaying time of about 18 ps. Such a relaxation time is typical for electron–phonon interacting subsystems [15]. Therefore, the temperature behaviour of the observed PISHG signal should be related to a phase transition described by the anharmonic electron–phonon interactions. However, skutterudite compounds have a centrosymmetric structure, so that the non-linear optical phenomena described by third rank polar tensor components should be forbidden by symmetry. The nature of the observed effect may be explained only by disturbances of the centrosymmetry by near-the-surface photoinduced treatments.

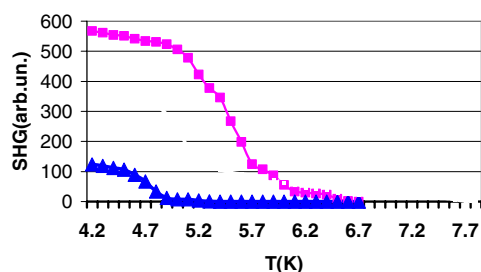


Figure 2. Typical temperature dependence of PISHG for: (▲)— $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$; (□)— $\text{CeFe}_4\text{Sb}_{12}$.

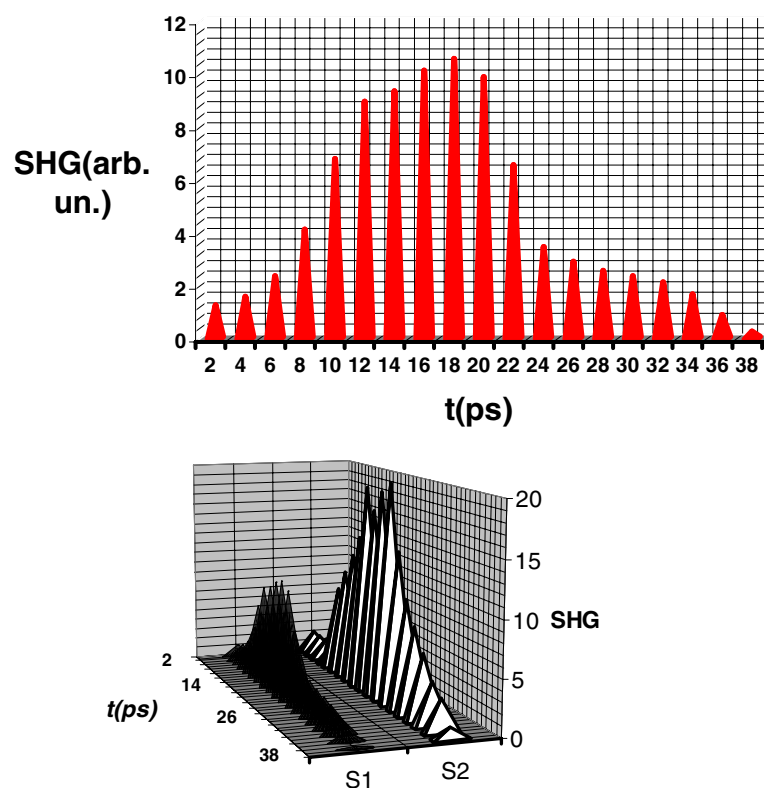


Figure 3. (a) Time evolution of the PISHG for $\text{CeFe}_4\text{Sb}_{12}$. (b) Comparison of time evolution for two compounds: (S1) $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$; (S2) $\text{CeFe}_4\text{Sb}_{12}$.

We have excluded a hypothesis that the PISHG signal could be due to the presence of CeSb_2 in these two compounds because our magnetic susceptibility and scanning electron microscope measurements performed in the $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ sample show no presence of CeSb_2 contrary to the $\text{CeFe}_4\text{Sb}_{12}$ case [14]. In addition, the PISHG signal should appear above 15 K since CeSb_2 is a ferromagnetic compound with Néel temperature $T_C = 15$ K [16].

In figure 4, we present the magnetic field PISHG dependence versus the pump–probe delaying time for the $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ material. The influence of the magnetic field is demonstrated by the increase of the PISHG with increasing magnetic field (up to 2 T) and

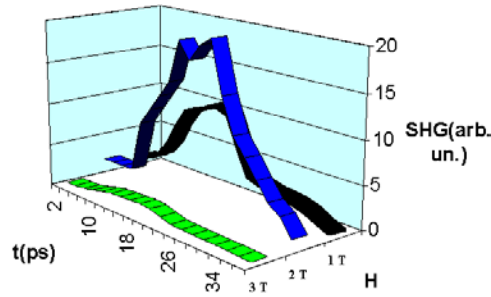


Figure 4. Magnetically dependent time evolution of the PISHG for $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$.

the drastic decrease afterwards (at about $H = 3$ T). The same behaviour was observed for $\text{CeFe}_4\text{Sb}_{12}$. Such a magnetic dependence of the PISHG is different from the dependence for ferromagnetic and superconducting [9–11] systems.

$\text{CeFe}_4\text{Sb}_{12}$ is a moderate HFC. In the HFC, there is coexistence between RKKY interaction (generally antiferromagnetic) and Kondo effect [17]. Maybe, these two combined effects cause the observed magnetic field dependence of the PISHG signal. Unfortunately, up to now, no PISHG experiment is known for antiferromagnetic materials. We believe that such data are necessary to understand and explain our experimental data.

There are two possibilities concerning the temperature dependence of $\text{CeFe}_4\text{Sb}_{12}$. First, Gajewski *et al* [8] have found a small peak at 1.5 K in C_p/T temperature dependence, although the origin of this peak is not clear. A hypothesis of magnetic impurities is not probable because the magnetic entropy between 0.4 and 1.5 K is approximately 10% of $R \ln 2$. If this peak has an intrinsic origin, the PISHG signal could be connected with this transition since the change of the PISHG should appear at higher temperatures than the one evaluated using other methods [9–12], in particular, the heat capacity.

Second, drastic changes of the electron density of states at the Fermi level occur in the HFC, roughly below the Kondo temperature T_K , because of a periodicity effect of the Kondo impurity lattice. As a result, the progressive appearance of a pseudogap in the Kondo resonance at the Fermi level is observed with decreasing temperature. Therefore, for low temperatures ($T \ll T_K$) where a renormalization of the conduction electron band is achieved, a heavy fermion band appears at the Fermi level [18, 19]. Although these changes of electron structure should not be associated by a phase transition like a λ one in heat capacity, we can expect the possible appearance of the strong anharmonic electron–phonon interaction related to the heavy fermion band [19] and connected with the PISHG signal. Indeed, Gerber *et al* [20] have considered the case of intermediate valence RE impurities. In this case, the large electronic density of states at the Fermi level $D(E_F)$ (due to hybridised 4f electrons) generates the very strong electron–phonon interaction as opposed to the weak classical electron–phonon interaction. In the case of the impurity lattice, the electron–phonon interaction should increase further by the coherence effect of the lattice. Moreover, since $D(E_F)$ is larger in the HFC than in the intermediate valence system, the electron–phonon interaction should still increase. This is observed in our compounds. The formation of the heavy Fermi liquid may modify the electron–phonon interaction and give rise to the signal, but the coherence temperature for $\text{CeFe}_4\text{Sb}_{12}$ is around 100 K [8]. So the heavy Fermi liquid is formed at higher temperatures than that at which the PISHG signal appears. At the same time there exists an upturn in parameter γ at $T \simeq 6$ K, of unknown origin. One can expect that this factor may give an additional contribution to the observed behaviour of the PISHG.

It should be noted that $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ has not been investigated to a great extent. Our preliminary magnetic susceptibility and resistivity measurements [14] have revealed behaviour similar to that of $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ [8], although with a smaller upturn at low temperatures. This is in accordance with the lower cerium concentration in the nickel-based compound. We can expect the heavy fermion behaviour in this compound to be similar to $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$. The latter hypothesis can explain why the magnetic field dependence of the pump–probe delaying time of $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ is similar to that one of $\text{CeFe}_4\text{Sb}_{12}$. More experimental data are necessary for a better understanding of the origin of the PISHG signal in this compound. In fact, heat capacity measurements are being performed, although above 3 K.

Since the behaviour of these compounds is very complex and not quite clear, it is necessary in future to perform a PISHG experiment using the well-characterised HFC to determine the physical origin of the PISHG signal in the skutterudite compounds studied in the present report.

4. Conclusion

The PISHG study of a compound showing moderate heavy fermion behaviour was performed. The PISHG signal appears only at 6.8 and 4.9 K for $\text{CeFe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.7}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$, respectively. The formation of the heavy Fermi liquid may modify the electron–phonon interaction and give rise to the signal, however the temperature for $\text{CeFe}_4\text{Sb}_{12}$ is around 100 K. So the heavy Fermi liquid is formed at higher temperatures than that at which the PISHG signal appears. At the same time the observed upturn in parameter γ at $T \approx 6$ K [8] may be a more important factor in the observed temperature behaviour. Unfortunately, the compounds studied have not been sufficiently investigated to date. Therefore, it is necessary to perform the PISHG experiment on a nonmagnetic prototypical HFC like CeCu_6 and an antiferromagnetic prototypical HFC like CeAl_2 to determine the physical origin of the PISHG signals. Such experiments could improve our knowledge concerning the electron–phonon interactions in the HFC's, in general, and the physical properties of $\text{CeFe}_4\text{Sb}_{12}$, in particular.

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