

Calorimetric absorption spectroscopy at mK temperatures – an extremely sensitive method to determine nonradiative processes in solids

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Any absorption of radiation followed by nonradiative transitions increases the temperature of the excited medium. The measurement of the sample temperature as a function of the excitation wavelength is known as calorimetric absorption spectroscopy (CAS), and its sensitivity increases with decreasing temperature. We describe here a sample/thermometer arrangement allowing quantitative CAS measurements in the mK range using a $^3\text{He}/^4\text{He}$ dilution refrigerator for the detection of nonradiative processes in solids with an extreme sensitivity. The application of CAS in the mK range is demonstrated by measurements on Ni-doped CdS crystals. The determination of the quantum efficiency of inner impurity transitions becomes now possible, leading to new information on the relaxation and recombination processes of the excited impurity ion.

1. Introduction

In semiconductor research, enhanced efforts are made in the investigation of nonradiative processes, as they influence strongly the electrical and optical properties of the samples and are therefore decisive for possible applications in optoelectronics. One experimental method for the determination of nonradiative processes is the calorimetric absorption spectroscopy (CAS) which was first used to characterize semiconductors by Bimberg and Bubbenzer in 1981 [1] and which turned out to be at low temperatures more sensitive than other photothermal techniques like photoacoustic absorption spectroscopy (PAS) [2,3] or photothermal deflection spectroscopy (PDS) [4].

The sensitivity of CAS increases drastically with decreasing temperature as a consequence of the temperature dependence of the specific heat and of the increasing sensitivity of resistance thermometers [5,6]. While Gruhl et al. [7] already used CAS in the mK range for investigation on dye molecules, this method was applied to semiconductor research only down to ^3He temperatures (0.5 K) [6]. For the first time, we present an experimental setup for quantitative CAS meas-

urements in the mK range, which allows us to determine the quantum efficiency of the excited states of solids by comparison of the heat power dissipated within the sample with the absorbed light power.

2. Calorimetric absorption spectroscopy

Nonradiative processes occur during the relaxation of an excited system to thermal equilibrium by the emission of phonons leading to an increase of the sample temperature. CAS is the measurement of this temperature and therefore leads to an integral detection of the emitted phonons.

The basic principle of CAS is the following: the investigated sample is thermally isolated within the vacuum chamber of a cryostat. It is monochromatically illuminated, and by nonradiative processes a fraction of the absorbed light is dissipated into heat leading to a rise of the sample temperature. The best way to measure this temperature is to attach the thermometer directly to the sample, but in this case the problem arises that the thermometer is illuminated by scattered light or luminescence and would thus falsify the

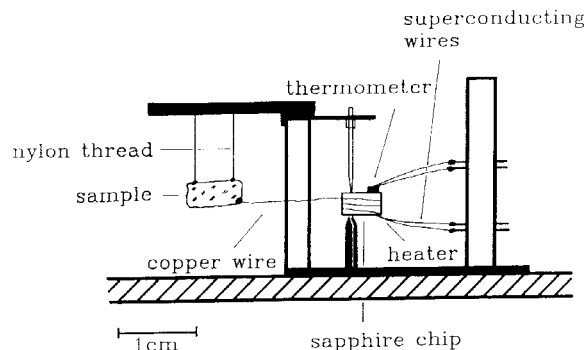


Fig. 1. Sample/calorimeter arrangement for CAS at mK temperatures. The setup is located within the vacuum chamber of a dilution refrigerator.

CAS signal. Instead, the thermometer is attached a few centimeters apart from the sample, protected from radiation, and coupled thermally to the sample. A CAS spectrum is taken by tuning the wavelength of the irradiated light and by measuring simultaneously the change of the sample temperature.

2.1. Sample/calorimeter arrangement for CAS at mK temperatures

The basic idea of the sample/calorimeter arrangement for CAS at mK temperatures is taken from the initial work of CAS at low temperatures by Juhl and Jeiter and is described in detail in refs. [5,6]. For the work in the mK range it was necessary to modify it considerably, as experimental requirements change drastically when the temperature is decreased from the K to the mK range.

The experimental setup within the cryostat is shown in fig. 1. The sample is fixed in vacuum by nylon threads with an extremely low thermal conductivity to enhance the thermal isolation of the sample. A sapphire chip serves as support for the thermometer. Sapphire is very suitable due to its small heat capacity and large thermal conductivity. While the sample is thermally well coupled to the sapphire chip by a 50 μm copper wire, the calorimeter is connected to the basic temperature of the cryostat via a thermal link leading to a temperature difference between sample/calorimeter

and the reference temperature of the cryostat. The thermal link results from the acoustic mismatch between sapphire and copper which depends on the connecting area and the pressure between the two materials. It is realized by putting the sapphire chip on thin copper pillars. So the thermal link can easily be varied by turning the plastic screw which fixes the sapphire chip onto the copper pillars. A heater consisting of a thin gold film is evaporated on the back side of the sapphire chip to calibrate the CAS signal. It enables us to measure quantitatively the heat power produced in the sample. The electric connections of the thermometer and the heater are made by superconducting NbTi wires to ensure that no heat can flow via the electric contacts.

The thermometer consists of a RuO_2 film on a ceramic substrate. It is mounted on the sapphire chip by a thin film of silver paint or "GE varnish" low-temperature adhesive. Ruthenium oxide (RuO_2) turned out to be a very suitable material because it shows a drastical increase of resistance below ca. 0.3 K and can be used down to a few mK [8]. The resistance change of the RuO_2 thermometer is measured with a low-power resistance bridge (AVS-46, Elektronikka Oy, Finland).

To obtain temperatures in the mK range, a commercial $^3\text{He}/^4\text{He}$ dilution cryostat (Oxford Instruments, UK) is used which allows one to hold the temperature around 40 mK for several weeks. The CAS arrangement (fig. 1) is mounted within the vacuum chamber of the cryostat. Due to its windowless construction, light has to be brought to the sample via optical fibers. As light source, a tungsten lamp is used in combination with a 0.75 m grating spectrometer to decompose the light irradiated onto the sample.

2.2. Temperature dependence of CAS

The temperature rise of the sample is measured as a change of the electrical resistance R of the thermometer. Its relative sensitivity G is given by

$$G = \frac{1}{R} \frac{\Delta R}{\Delta T}, \quad (1)$$

and so the relative resistance change $\Delta R/R$ is

$$\frac{\Delta R}{R} = \frac{1}{R} \frac{\Delta R}{\Delta T} \Delta T. \quad (2)$$

A thermal circuit diagram to describe the temperature dependence of the CAS signal for our sample/thermometer arrangement was developed by Juhl and is analyzed in detail in ref. [5]. The main aspect is that the temperature difference depends on the produced heat power Δp and the thermal resistance R_L of the thermal link

$$\Delta T = R_L \Delta p, \quad (3)$$

$$\Delta R/R = G R_L \Delta p. \quad (4)$$

Thus the CAS signal can be enlarged by increasing the thermal resistance, but one has to recognize that also the time constant of the system depends on the thermal resistance:

$$\tau = C_p R_L, \quad (5)$$

$$\frac{\Delta R}{R} = \frac{G \tau}{C_p} \Delta p. \quad (6)$$

The time constant does not vary significantly with decreasing temperature, because the thermal resistance resulting from the acoustic mismatch is proportional T^{-3} ("Kapitza problem"), while the specific heat is decreasing due to the Debye law for crystalline solids proportional to T^3 .

The CAS signal only depends on the sensitivity of the thermometer and the specific heat of the sample/calorimeter arrangement and therefore increases drastically with decreasing temperature. Fig. 2 shows the increase of the CAS signal with decreasing temperature, using as an example the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ absorption of Ni impurities in CdS. The signal increases by a factor of 220 when the basic temperature decreases from 150 to 45 mK. This corresponds well to the product of the increase of G (factor 12) with R_L (factor 18) according to eq. (4). Thus it is obvious that CAS experiments should be performed at minimum base temperature to get an optimal CAS signal.

2.3. Sensitivity of CAS at mK temperatures

According to eq. (4), the sensitivity $\Delta R/R$ of the calorimeter depends on the thermal resis-

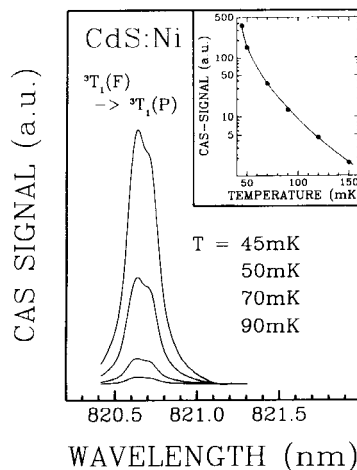


Fig. 2. CAS spectra of the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ Ni^{2+} absorption at different temperatures. The insert shows the temperature dependence of the CAS signal.

tance R_L and the relative sensitivity of the thermometer. But, of course, it also depends on the resolution of the resistance bridge which in our case is $\Delta R/R = 10^{-4}$. At $T = 45$ mK, $G = 68 \text{ K}^{-1}$ and $\Delta R/R = 10^{-4}$. So the smallest measurable temperature difference amounts to

$$\Delta T = \frac{1}{G} \frac{\Delta R}{R} = 1.5 \mu\text{K}.$$

Assuming a typical thermal resistance of $150 \text{ K}/\mu\text{W}$, a minimum heat power of

$$\Delta p = \Delta T/R_L = 10 \text{ fW}$$

can be detected.

However, even more important than the theoretical resolution is the lowest experimentally detectable heat power which is limited by noise. Different noise sources produce heat in the sample/calorimeter or even in the whole cryostat, leading to a background heating of the whole arrangement and would result in a reduced sensitivity. There are three main noise sources which one has to take care to minimize. First, there are vibrations caused by the different pumps which are necessary to run the cryostat, and vibrations may also arise from building resonances. The second main noise source is RF radiation, because all electric lines serve as aerials and so RF

Table 1
Comparison of CAS parameters at 1.3, 0.5 and 0.045 K with a similar sample/thermometer arrangement

Temperature	Thermometer	Sensitivity (K ⁻¹)	ΔP_{\min} (theor.) (pW)	ΔP_{\min} (exp.) (pW)
⁴ He (1.3 K)	Carbon	5	10	250
³ He (0.5 K)	Germanium	8.5	4	20
³ He/ ⁴ He (0.045 K)	RuO ₂	68	0.01	0.1

radiation induces a small voltage leading to the production of heat in the cryostat. This heat power may only be a few pW but even this is much more than the theoretical resolution of 10 fW at 45 mK. A third noise source is the thermal 300 K background radiation which enters the cryostat via optical windows.

In our case we have been able to minimize the influence of the noise sources. The vibrations are reduced by leading all pumping lines through a large box filled with sand providing a very efficient decoupling of the pumping vibrations. The largest noise source – RF radiation – is completely eliminated by locating all the electrical equipment within a RF-shielded “Faraday cage”. The thermal background radiation does not disturb our CAS measurements because of the windowless construction of the dilution cryostat.

All these noise-reducing activities lead to a low noise level of less than $\Delta R/R \approx 10^{-3}$, so we are able to detect a minimum heat power of 100 fW. This value has to be seen in comparison to the parameters from ⁴He and ³He CAS experiments achieved with a similar sample/calorimeter arrangement (table 1) and to the value of 2 pW reported from Gruhl et al. [7] for their CAS system at 30 mK.

3. Detection of low absorption by CAS

As we have seen, the lowest detectable heat power is 100 fW in our case, a value which has to be compared with the highest possible irradiation power limited by the cooling power of the cryo-

stat (about 0.7 μ W at 45 mK). So the lowest detectable αd product – which also depends on the quantum efficiency because CAS detects only the nonradiative part of the absorption – becomes

$$\alpha d = \Delta P_{\min}(\text{CAS}) / \Delta P_{\max}(\text{in}) = 1.5 \times 10^{-7}$$

if the quantum efficiency is set to zero to get the lower limit. But even if the quantum efficiency is 99%, absorption of less than 0.1% can still be detected.

4. Calorimetric transmission spectroscopy (CTS) for the determination of quantum efficiencies

By using CAS, we measure the heat power produced in the sample, information which is not available by any other experimental technique. So it is now easily possible to determine the quantum efficiency of the absorption, i.e. the ratio of radiative to nonradiative decay, knowing the light power absorbed in the sample. This is determined by putting a black body realized by a black-painted copper foil directly behind the sample, and to measure the transmitted light power by a second calorimeter.

By simultaneous calorimetric measurements of absorption and transmission, it is now possible to determine the quantum efficiency in absolute values, because CAS only detects the *nonradiative* processes during the relaxation to thermal equilibrium, while CTS measures the total absorbed light power leading to *radiative and nonradiative* processes.

The quantum efficiency η is defined

$$\eta = 1 - \Delta P_{\text{nr}} / \Delta P_{\text{nr+r}}, \quad (7)$$

where $\Delta P_{\text{nr+r}}$ is the total absorbed light power and ΔP_{nr} is the heat power produced in the sample by nonradiative processes (r = radiative, nr = nonradiative).

The total absorbed light power can be concluded from CTS by the formulas

$$\Delta P_{\text{CTS}} = P_{\text{in}} \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}}, \quad (8)$$

$$\Delta P_{nr+r} = P_{in} \frac{(1-R)(1-e^{-\alpha d})}{1-R e^{-\alpha d}}, \quad (9)$$

which can be derived from simple geometric considerations. From eq. (8) the product αd can be determined by estimating the quantum efficiency for the background absorption, and then from eq. (9), ΔP_{nr+r} follows. The reflection coefficient R is taken from the literature. Because ΔP_{nr} is directly measured in the CAS experiment, one can now determine the quantum efficiency.

5. Example: quantum efficiency of inner impurity transitions of CdS: Ni

As an example for the application of CAS in combination with CTS, we demonstrate the determination of the quantum efficiency of the ${}^3T_1(P) \rightarrow {}^3T_1(F)$ transition of Ni^{2+} in CdS. Fig. 3 shows the CAS spectrum and the totally absorbed light power ΔP_{nr+r} , calculated from the CTS spectra. Four lines $O_{1,2}$ and $S_{3,4}$ according to the fine structure of the upper ${}^3T_1(P)$ level [9] can be observed.

From the data depicted in fig. 3, the quantum efficiency of the ${}^3T_1(P)$ level of Ni^{2+} in CdS can be deduced to be 22%. But, of course, this does

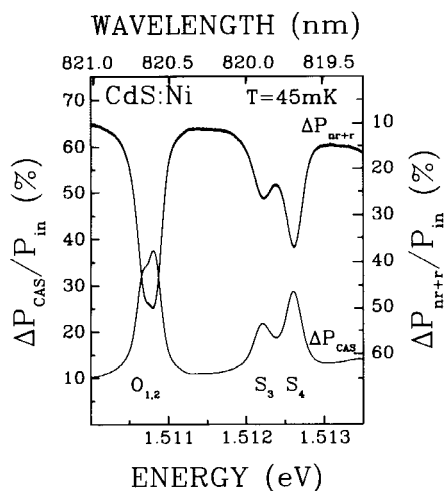


Fig. 3. CAS spectrum of the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ Ni^{2+} absorption in CdS in comparison to the absorbed light power ΔP_{nr+r} calculated from the CTS spectrum.

not mean that exactly 22% of the excited charge carriers recombine radiatively directly to the ground state leading to the ${}^3T_1(P) \rightarrow {}^3T_1(F)$ luminescence and 78% recombine via the emission of phonons, because one has to take into account the relaxation via lower electronic states, as ${}^3A_2(F)$ and ${}^3T_2(F)$. For example, there might be a nonradiative relaxation from ${}^3T_1(P)$ to ${}^3A_2(F)$, leading to a photon emission line at 1.2 μm . So, if exactly the relaxation and recombination processes are to be determined it is necessary to measure the quantum efficiency of each electronic level separately.

A more detailed report on experimental results concerning nonradiative relaxation and recombination processes of Ni impurities in different II–VI semiconductors is given in ref. [10].

6. Conclusion

We presented an improved sample/calorimeter arrangement for calorimetric absorption spectroscopy. Decreasing the temperature down to the mK range by using a ${}^3He/{}^4He$ dilution refrigerator has led to an extreme sensitivity of the CAS setup, and the lowest detectable heat power amounts to 100 fW at 45 mK.

The two main applications of CAS are (1) the detection of low absorptions and (2) the determination of quantum efficiencies by a simultaneous calorimetric measure of the transmission.

The possibility to determine quantum efficiencies in absolute values adds a new dimension to the investigation of relaxation and recombination processes of excited states, especially in combination with excitation spectroscopy which detects radiative and nonradiative relaxation to an electronic state, while CAS/CTS determines the ratio of radiative to nonradiative decay of the excited state.

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References

- [1] D. Bimberg and A. Bubbenzer, *Appl. Phys. Letters* 38 (1981) 803.
- [2] Y.H. Pao, *Optoacoustic Spectroscopy and Detection* (Academic Press, New York, 1977).
- [3] R. Kuhnert and R. Helbig, *Appl. Opt.* 20 (1981) 4149.
- [4] W.B. Jackson, N.M. Amer, A.C. Boccara and D. Fournier, *Appl. Opt.* 20 (1981) 1133.
- [5] A. Juhl and D. Bimberg, *J. Appl. Phys.* 64 (1988) 303.
- [6] D. Bimberg, T. Wolf and J. Böhrer, in: *Proc. NATO ASI Conf. on Advances in Nonradiative Processes in Solids, 1989*, in NATO ASI Series (Plenum, New York, in press).
- [7] H. Gruhl, H.-P. Dorn and K. Winzer, *Appl. Phys. B* 38 (1985) 199.
- [8] R.W. Willekers, F. Mathu, H.C. Meijer and H. Postma, *Cryogenics* 30 (1990) 351.
- [9] I. Broser, A. Hoffmann, R. Germer, R. Broser and E. Birkicht, *Phys. Rev. B* 33 (1986) 8196.
- [10] L. Podlowski, R. Heitz, A. Hoffmann and I. Broser, in: *Proc. 8th Intern. Conf. on Dynamical Processes in Excited States of Solids (DPC '91)* (J. Luminescence, to be published).