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Latent heat evaluation with photopyroelectric calorimetry

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Abstract. A high resolution ac photopyroelectric calorimeter has been used to provide qualitative information on latent heat exchange and so establish the character of phase transitions in solids. Antiferromagnetic to paramagnetic transition in CoO is shown to present a small heat exchange characteristic of a weak first order transition. Well known first and second order transitions in KFeF₄ and NiO, respectively, are studied as a contrast method.

1. Introduction

Photopyroelectric calorimetry (PPE) is a technique widely used to study the dynamical properties of phase transitions in solids and liquids, because of its high resolution and sensitivity [1-4]. The ac PPE technique is specially suited to study the thermal properties around phase transitions, since small temperature gradients in the samples produce a high signal-to-noise ratio. Performing the measurements at low temperature rates, a detailed study in the close vicinity of the transitions can be obtained; thus, PPE calorimetry has enabled the determination of the critical behaviour of second-order phase transitions in magnetic and ferroelectric materials [5-11]. On the other hand, as exchanged latent heat in a first order transition can not be measured directly with this technique, it is commonly believed that it is not useful to establish the character of a transition. Nevertheless, ac calorimetric techniques have already been used to determine the character of transitions because an indirect evaluation of latent heat can be obtained [12]. In particular, PPE calorimetry has been lately applied to this evaluation in the case of liquid crystals [13,14]. These studies have shown the presence of heat flow and have contributed to the attribution of a first-order character to the transitions.

In this work we are extending this procedure to the evaluation of latent heat in phase transitions in solid samples. To start with, we have tested it for the case of two well-known phase transitions: KFeF₄, which presents a first order structural transition at 388.2 K, with space groups Amma at high temperature and Pmcn at low one, and NiO, which shows a well known second order antiferromagnetic to paramagnetic transition at about 522 K. Lastly, another transition metal oxide has been studied: CoO, with an antiferromagnetic to paramagnetic transition at about 287.7 K and whose character is doubtful. Renormalization-group theory supports that it should have a first-order nature [15]. On the other hand, experimental results in the past have pointed to a second order character [16-18] while recent photopyroelectric measurements performed by the authors' group point to a weak first order character, which is only shown in the samples with the best crystallographic quality [19]. In the three cases studied now, all samples are high quality single crystals. Thus, the aim of this work is to ascertain the powerfulness of the technique and the limits of the physical model involved to evaluate latent heat exchange (and so, the character of the transition) in the case of solids.

2. Fitting results and discussion

To achieve this purpose, experimental measurements have been performed with an ac photopyroelectric calorimeter (the details of the experimental procedure can be found in ref. [10], for instance) and the standard model used to work out the thermal properties of the sample from the amplitude and phase of the photopyroelectric signal in the back detection configuration is modified. In the case of a thermally thick sample regime, the complex PPE signal, normalized to the one obtained on the bare photopyroelectric detector, reads [14]

$$V = \frac{\epsilon_p}{\epsilon_s + \epsilon_p} \left(e^{-\sigma l} + \frac{I_{\text{int}} e^{-j\Psi}}{\sigma} \right) \quad (1)$$

where j is the imaginary unit, $\epsilon = (K\rho c)^{1/2}$ is the thermal effusivity, subindexes p, s referring to pyroelectric detector and sample, respectively, ρ is the density, c is the specific heat, K is the thermal conductivity, $\sigma = (1+j)(\pi f/D)^{1/2}$, l is the sample thickness, f the modulation frequency and $D = K/\rho c$ is the sample thermal diffusivity.

The PPE signal in equation (1) is written as the addition of two terms: the first one corresponds to the signal obtained when an opaque sample is heated by the laser excitation and it is the usual contribution taken into account. For the case of first order transitions, where there is an exchange of latent heat, part of the PPE signal must have its origin in this new source of heat, thus forcing the addition of the second term, which must be negligible in the case of second-order transitions. This new source is modeled as a delayed source uniformly distributed in the sample volume, with an amplitude I_{int} and a phase lag Ψ . The experimental amplitude and phase are simultaneously fitted with this model to obtain a thermal property (either specific heat or thermal diffusivity) and the amplitude of the internal source I_{int} , thus assessing the presence or not of a latent heat. In order to apply this model without increasing the number of unknown parameters, thermal conductivity profile $K(T)$ as a function of temperature must be introduced as a known quantity. This means that this is a sound method if there is no singularity in K at the critical temperature (which is known to be true for most materials). In order to avoid scattering of the data, the phase lag Ψ was kept constant throughout the transition; its value was then progressively varied as an external parameter so as to optimize the fit with the experimental results.

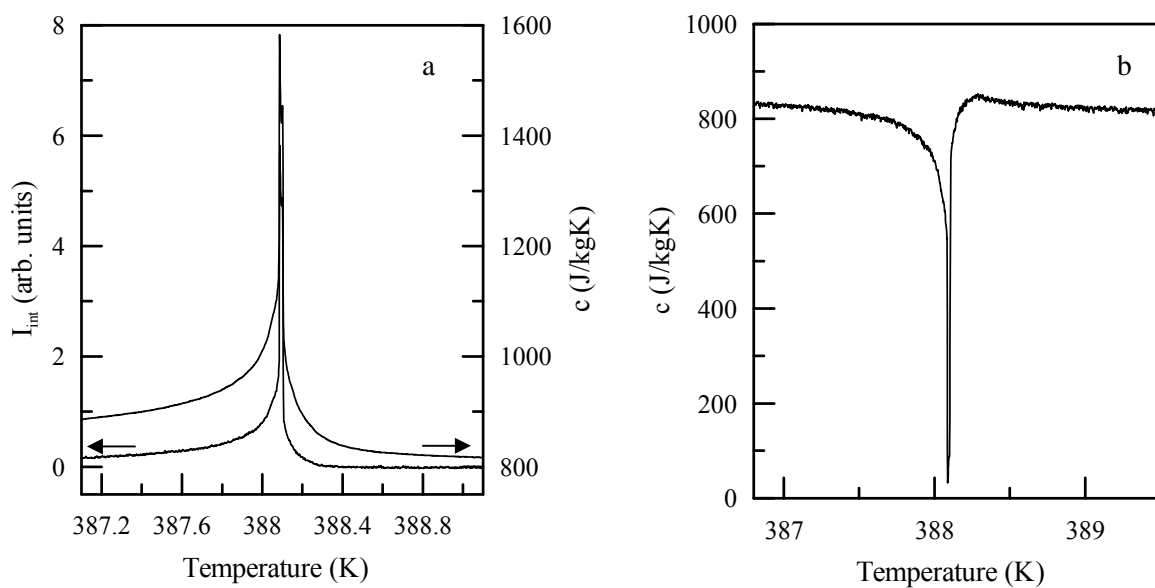


Figure 1. **a)** Internal heat source amplitude I_{int} and specific heat c for KFeF_4 ; **b)** Specific heat c obtained fitting only with the first term in equation (1), for KFeF_4 .

Figure 1a shows the fitted values obtained for the internal heat source $I_{\text{int}}(T)$ and specific heat $c(T)$ in the case of KFeF_4 . An arbitrary scale is taken for $I_{\text{int}}(T)$, as the information it provides is only of a qualitative nature. There are narrow peaks in both magnitudes, as there must be in the case of a first order transition. What is even more interesting is that, for this material, there is no way of obtaining a specific heat with physical sense if the latent heat source were not taken into account in the fitting. Figure 1b shows the specific heat obtained fitting the amplitude and phase only to the first term of equation (1), even allowing K to vary as another fitting parameter. The shape of the specific heat is devoid of any physical meaning.

Figure 2 shows the fitted values for $c(T)$ and $I_{\text{int}}(T)$ in the case of NiO . As expected for the case of a second order phase transition, the contribution of the latent heat source term is negligible.

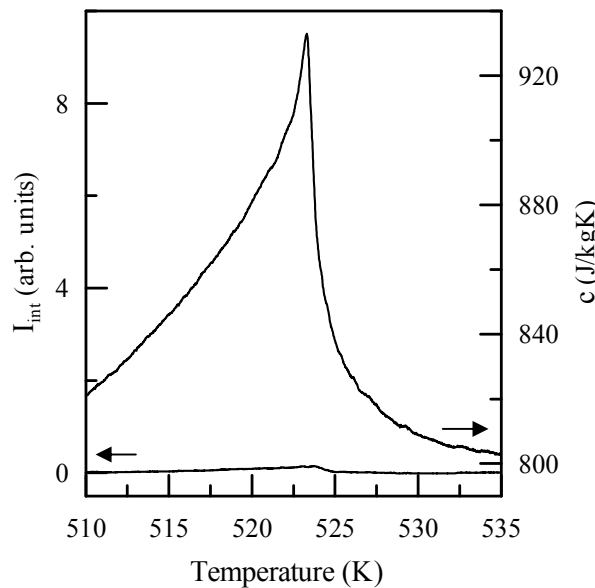


Figure 2. Internal heat source amplitude I_{int} and specific heat c for NiO .

Lastly, figure 3 shows the results for CoO ; in this case, there is a narrow and sharp specific heat curve, while there is a small peak for the internal heat source. It indicates the presence of exchanged heat, though in a small quantity, showing that the magnetic transition in CoO is weak first order. As this result is only obtainable in a high quality single crystal sample, and not in any single crystal, this suggests that the true character of the transition was not revealed in previous measurements in literature because surely the crystalline quality of the samples was not good enough.

It is worth noting the important role of the phase lag Ψ in equation (1), which expresses the delay between the heat sources, because the results depend heavily on its value. As an example, figure 4 shows the fitted specific heat curves which correspond to three different phase lags values a) $\Psi = 3$ rad, b) $\Psi = 3.54$ rad and c) $\Psi = 6$ rad. Curves a) and c) have clearly no physical sense. Around the best value of 3.54 rad in curve b) there is a bunch of values which also give sensible results both for specific heat and heat source, being difficult to establish a criterium to select which is the best one, and so introducing an indetermination. On the other hand, this is not a severe issue, as this method gives a qualitative and not quantitative evaluation of latent heat.

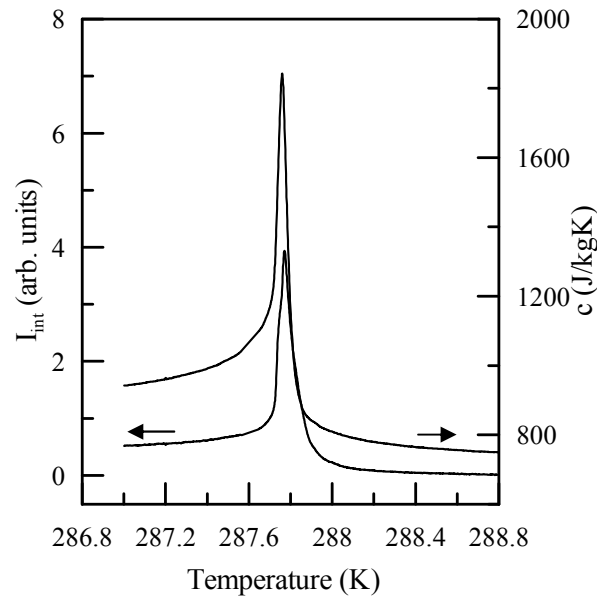


Figure 3. Internal heat source amplitude I_{int} and specific heat c for CoO.

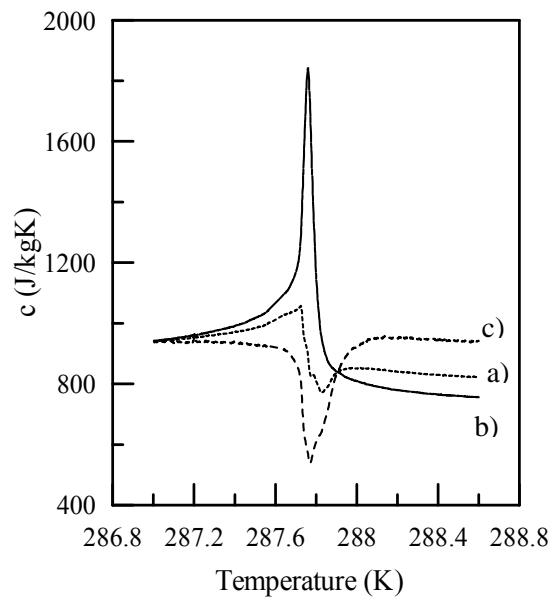


Figure 4. Specific heat c obtained for three different values of the phase lag a) $\Psi = 3$ rad, b) $\Psi = 3.54$ rad and c) $\Psi = 6$ rad, for CoO.

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