

**Latent heat at the magnetic transition in CoO**A. Oleaga,<sup>1</sup> A. Salazar,<sup>1</sup> and E. H. Bocanegra<sup>2</sup><sup>1</sup>*Departamento de Física Aplicada I, Escuela Técnica Superior de Ingeniería, Universidad del País Vasco, Alameda Urquijo s/n, 48013 Bilbao, Spain*<sup>2</sup>*Departamento de Física Aplicada II, Facultad de Ciencia y Tecnología, UPV/EHU, Apartado 644, 48080 Bilbao, Spain*  
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The character of the transition that takes place at the Néel temperature in CoO, from a cubic paramagnetic phase to a monoclinic antiferromagnetic one, has been studied through the evaluation of the exchange of latent heat. A high-resolution ac photopyroelectric calorimeter has been used to provide qualitative information on this issue, measuring high quality single crystal samples. The results show the presence of a small heat exchange characteristic of a weak first order transition.

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**I. INTRODUCTION**

Transition-metal magnetic monoxides MnO, FeO, CoO, and NiO have been studied along the last forty years. MnO, FeO, and NiO have in common that they all crystallize with the NaCl structure (space group  $Fm\bar{3}m$ ) in their high-temperature state and are type-II antiferromagnets in the low-temperature one: the magnetic spins align ferromagnetically within the (111) plane while these planes are stacked antiferromagnetically in the direction normal to the (111) plane. At their respective Néel temperature they undergo a paramagnetic to antiferromagnetic phase transition coupled to a symmetry breaking consisting of a small rhombohedral distortion along the [111] direction, thus the symmetry of the lattice is fully consistent with the magnetic structure.<sup>1</sup> In the case of CoO, recent studies have shown that the transition is more complex than it was thought and that some of its features were still to be revealed. It has been traditionally considered a type-II antiferromagnet with the same kind of spin alignment as in the rest of the family but with a tetragonal lattice distortion along the [001] direction arising at the Néel temperature.<sup>1</sup> In the last years, it has been shown, in the first place, that the lattice distortion has also a monoclinic component and so the symmetry of the low-temperature phase is lowered<sup>2</sup>; second, that the type-II antiferromagnetic order coexists with a type-I antiferromagnetic structure (in which ferromagnetic (001) planes are stacked along the tetragonal [001] axis), giving rise to a monoclinic magnetic structure in agreement with the lattice symmetry previously proposed.<sup>3</sup>

Concerning the character of this transition, renormalization-group analysis performed in the seventies suggested that the magnetic phase transition in the four transition-metal monoxides should have a first-order nature.<sup>4-6</sup> This has been experimentally confirmed in the case of FeO and MnO (Refs. 7–12) though in this last case its first-order character was not revealed with polycrystalline samples and not even in every single crystal of this material. The first-order character was confirmed using particular single crystal samples or single crystals to which a stress in the [111] direction was applied, the effect of this stress being to eliminate all but one of the magnetic domains.<sup>7,10</sup> On the other hand, the transition in NiO is clearly second order<sup>13-15</sup>; its critical behavior has lately been shown to belong to the Heisenberg universality class.<sup>16</sup>

Lastly, CoO has been traditionally considered to be second order according to different types of experimental measurements,<sup>17-23</sup> though recent high-resolution measurements performed by our group by means of an ac photopyroelectric (PPE) calorimeter show that the shapes and features of the thermal properties (specific heat and thermal diffusivity) in the close vicinity of the Néel temperature depend heavily on the particular sample used, even if all of them are single crystals.<sup>16</sup> The crystalline quality of the samples under study has been assessed by neutron diffraction measurements and a direct relationship found between the quality of each sample and the sharpness of the singularities obtained by its study. In the close vicinity of the critical temperature, the poorest quality samples gave rounded peaks with the same shape as those that can be found in literature; it is from this kind of data that a second-order nature had been claimed and specific universality classes assigned by other authors.<sup>21-23</sup> As we obtained sharper peaks, the values of the critical parameters moved away from any universality class, invalidating previous analysis and indicating that the picture is not as simple as thought. Though there are many second-order transitions for which no universality class is found or which present abnormal critical parameters, taking into account the results of renormalization-group theory, as well as the character of FeO and MnO, the possibility that the transition in CoO has a weak first-order character must be considered; this would not have been revealed up to now due to any combination of the following reasons: the particular samples used, the resolution of the measurements performed or the experimental techniques employed.

As latent heat exchange is one of the main issues in establishing the character of a transition, attention has been focused in this work on trying to establish the presence or absence of latent heat by means of ac PPE calorimetry, which is a technique well established to study the dynamical properties of phase transitions in solids and liquids,<sup>21,24-27</sup> due to its high sensitivity and resolution. The ac PPE technique is specially suited to study the thermal properties around phase transitions since small temperature gradients in the sample produce a high signal-to-noise ratio, which in combination with low-temperature rates allow to accurately study the close vicinity of the transitions. PPE calorimetry has enabled the determination of the critical behavior of second-order phase transitions in magnetic and ferroelectric

materials,<sup>27–34</sup> but it is generally believed not be useful to discriminate the character of a transition because of the limitation of obtaining the exchanged latent heat.

In spite of this limitation, ac calorimetric techniques have already been used to determine the character of transitions because an indirect evaluation of latent heat can be obtained.<sup>35</sup> In particular, PPE calorimetry has been lately applied to this evaluation in the case of liquid crystals,<sup>36,37</sup> showing the presence of heat flow in the transition, and thus contributing to the determination of their first-order character.

We have applied this approach to CoO with the aim of ascertaining the character of the magnetic transition. As a further check of the powerfulness of the evaluation of latent heat in transitions through high-resolution ac PPE calorimetry, other solid materials which present well-known first- or second-order transitions have also been measured with this technique in this work.

## II. EXPERIMENTAL SETUP AND SAMPLES

In order to obtain the specific heat profile as a function of temperature with high resolution, as well as to confirm latent heat exchange, a high-resolution ac PPE calorimeter has been used in the standard back-detection configuration.<sup>24,25</sup> An acousto-optically modulated He-Ne laser beam of 5 mW illuminates the front surface of the sample under study. Its rear surface is in thermal contact with a 350  $\mu\text{m}$  thick LiTaO<sub>3</sub> pyroelectric detector with Ni-Cr electrodes on both surfaces, by using an extremely thin layer of a highly heat-conductive silicone grease (Dow Corning, 340 Heat Sink Compound). Both sample and detector are placed inside a cryostat allowing measurements between 77 and 450 K, at rates that can be as low as 5 mK/min for high-resolution runs close to the phase transitions. The photopyroelectric signal is processed by a lock-in amplifier operating in the current mode and measurements have been performed in the thermally thick regime.

Single crystals have been used for this study in order to obtain shapes as sharp as possible for the transition peaks; the presence of grains, domains, or noncrystallinity introduce rounding in the thermal measurements at the critical temperature, which must be avoided at all costs to see the real features of the transition. It is widely known that to reveal the features and real character of a transition, high quality samples need to be employed (high purity, good stoichiometry, few defects, single crystals, ...). As it has already been pointed out, a fine example of this is the case of MnO, whose first-order character was finally revealed through the measurements of single crystal samples with the presence of a single magnetic domain.

In our previous study on CoO we used high purity single crystal samples coming from different growers to study and compare their thermal properties around the Néel temperature<sup>16</sup>, the one which led to more acute and sharper peaks (which happened to have the best crystallographic quality) has been used for this work. All samples are plane-parallel slabs with a thickness of the order of 0.5 mm and a diameter of about 6 mm.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

Regarding PPE measurements, for the experimental configuration used (back detection, thermally thick sample regime) the complex PPE signal (normalized to the one obtained on the bare photopyroelectric detector) reads<sup>37</sup>

$$V = \frac{\varepsilon_p}{\varepsilon_s + \varepsilon_p} \left( e^{-\sigma l} + \frac{I_L e^{-j\Psi}}{\sigma} \right) \quad (1)$$

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

The PPE signal in Eq. (1) contains two terms: the first one corresponds to the signal obtained when an opaque sample is heated by the laser excitation and the second one takes into account the effect of a delayed source uniformly distributed in the sample volume, holding for the latent heat exchange involved in a first-order transition, be it where the case. This source is modeled with an amplitude  $I_L$  and a phase lag  $\Psi$ . In the case of continuous transitions, this term would be negligible.

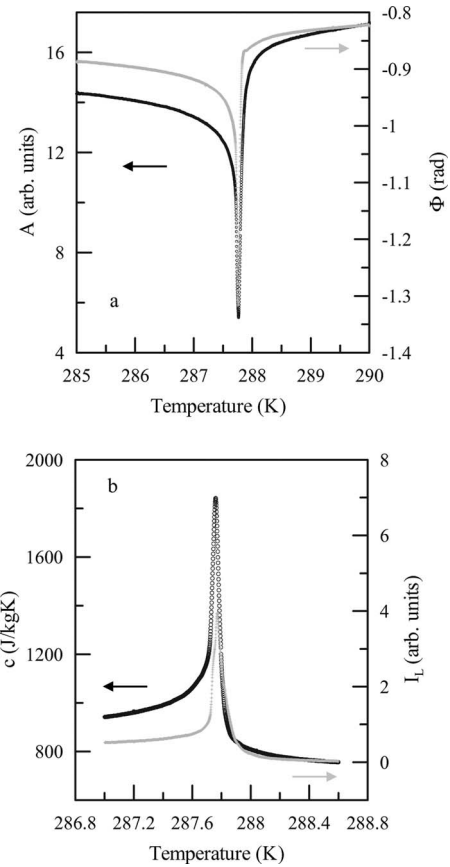


FIG. 1. (a) PPE signal amplitude  $A$  (black circles) and phase  $\Phi$  (gray crosses) over the antiferromagnetic-paramagnetic transition in CoO. (b) Fitted specific heat  $c$  (black circles) and amplitude of the latent heat term  $I_L$  (gray crosses) in a closer region around the transition temperature.

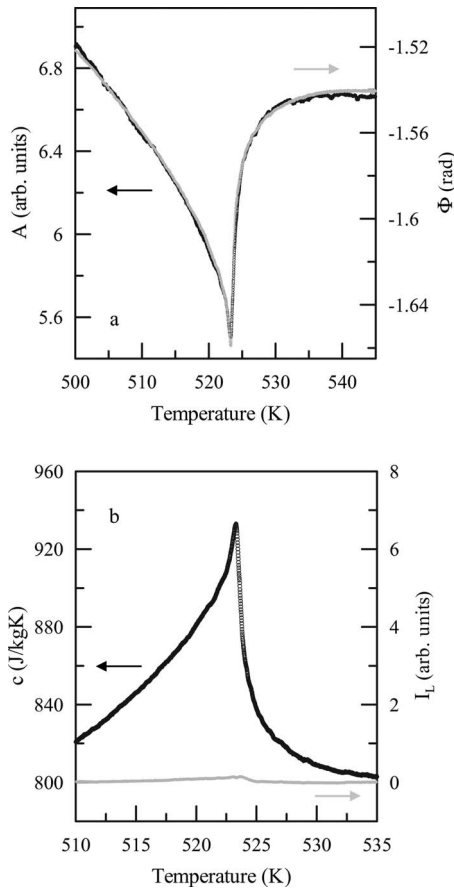


FIG. 2. (a) PPE signal amplitude  $A$  (black circles) and phase  $\Phi$  (gray crosses) over the antiferromagnetic-paramagnetic second-order transition in NiO. (b) Fitted specific heat  $c$  (black circles) and amplitude of the latent heat term  $I_L$  (gray crosses) in a closer region around the transition temperature.

Figure 1(a) shows the ac PPE measurements performed in the case of CoO, where the normalized amplitude  $A(T)$  and phase  $\Phi(T)$  of the PPE signal as a function of temperature are displayed. The experimental values so obtained were fitted at each temperature with those obtained from Eq. (1), with the specific heat  $c(T)$  and the amplitude of the internal source heat  $I_L(T)$  as fitting parameters, along the transition range. In order to avoid scattering of the data, the phase lag 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. As thermal conductivity does not present any singularity in the magnetic transition and it remains nearly constant in the near vicinity of it,<sup>16,21</sup>  $k$  has been taken as a uniform value. The fitted values obtained for specific heat  $c(T)$  and internal heat source  $I_L(T)$  are shown in Fig. 1(b). An arbitrary scale is taken for  $I_L(T)$ , as the information it provides is only of a qualitative nature.

The specific heat curve so calculated is narrow and sharp, while there is a small peak for the internal heating source. It indicates the presence of exchanged heat, supporting that the magnetic transition in CoO is not continuous and thus should be considered as weak first order; its character had been hidden in the samples used in the past for the measurements found in literature.

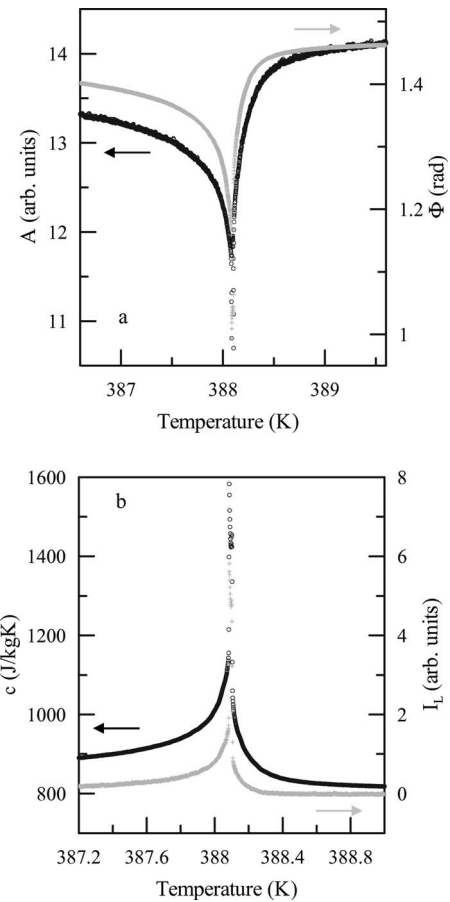


FIG. 3. (a) PPE signal amplitude  $A$  (black circles) and phase  $\Phi$  (gray crosses) over the first-order structural transition in KFeF<sub>4</sub>. (b) Fitted specific heat  $c$  (black circles) and amplitude of the latent heat term  $I_L$  (gray crosses) in a closer region around the transition temperature.

As it has been explained in the introduction, this method of evaluation of latent heat through PPE measurements has been applied up to now only to first-order transitions in liquid crystals. In order to further verify its powerfulness, other single crystal samples presenting well-known first- and second-order transitions in solids have also been studied so as to confirm the presence or absence of latent heat by means of this method. Figure 2(a) shows the experimental amplitude  $A(T)$  and phase  $\Phi(T)$  of the PPE signal for the case of the magnetic second-order transition in NiO while Fig. 2(b) displays the fitted specific heat  $c(T)$  and internal heat source  $I_L(T)$ . In the first place, it is worth noting how the experimental amplitude and phase have the same evolution with temperature, as expected for second-order transitions.<sup>37</sup> Besides, the fitted results give a negligible internal heating source corresponding to the second term in Eq. (1).

Lastly, a first-order transition was studied. We have measured a well-known first-order transition in a single crystal KFeF<sub>4</sub>, which takes place at 388.2 K. This is a structural phase transition, with space groups  $Amma$  at high temperature and  $Pm\bar{c}n$  at low one.<sup>38</sup> Figure 3(a) shows the experimental amplitude  $A(T)$  and phase  $\Phi(T)$  and Fig. 3(b) displays the fitted specific heat  $c(T)$  and internal heat source  $I_L(T)$ . Not only the specific heat curve is extremely sharp, as

corresponds to a first-order transition, but also an internal heating source amplitude is obtained, quite sharp and narrow. It is worth noting that, in this case, if the second term in Eq. (1) were not to be considered, the calculated specific heat results would be devoid of any sense.

As a conclusion, ac photopyroelectric calorimetry shows that heat is exchanged at the antiferromagnetic to paramagnetic transition in CoO, clearly indicating that this is not continuous, in opposition to the case of NiO. The qualitative characteristics of the internal heat source are not as marked as in an out-of-doubt first-order transition, therefore a weak first-order character can be attributed to this transition, which

is only identifiable in high quality single crystals samples. This implies that the critical parameter values that were obtained in our previous work in the different samples when dealing with CoO as if there was a continuous transition<sup>16</sup> are meaningless, only the result of curves too rounded to express the real character of the transition.

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- <sup>1</sup>W. L. Roth, Phys. Rev. **110**, 1333 (1958).  
<sup>2</sup>W. Jauch, M. Reehuis, H. J. Bleif, F. Kubanek, and P. Pattison, Phys. Rev. B **64**, 052102 (2001).  
<sup>3</sup>K. Tomiyasu, T. Inami, and N. Ikeda, Phys. Rev. B **70**, 184411 (2004).  
<sup>4</sup>S. A. Brazovskii and I. E. Dzyaloshinskii, Pis'ma Zh. Eksp. Teor. Fiz. **21**, 360 (1975) [JETP Lett. **21**, 164 (1975)].  
<sup>5</sup>P. Bak, S. Krinsky, and D. Mukamel, Phys. Rev. Lett. **36**, 52 (1976).  
<sup>6</sup>D. Mukamel and S. Krinsky, Phys. Rev. B **13**, 5078 (1976).  
<sup>7</sup>D. Bloch, R. Maury, C. Vettier, and W. B. Yelon, Phys. Lett. **49A**, 354 (1974).  
<sup>8</sup>D. Bloch, D. Hermann-Ronzaud, C. Vettier, W. B. Yelon, and R. Alben, Phys. Rev. Lett. **35**, 963 (1975).  
<sup>9</sup>R. Boire and M. F. Collins, Can. J. Phys. **55**, 688 (1977).  
<sup>10</sup>D. Bloch, C. Vettier, and P. Burlet, Phys. Lett. **75A**, 301 (1980).  
<sup>11</sup>M. S. Jagadeesh and M. S. Seehra, Phys. Rev. B **23**, 1185 (1981).  
<sup>12</sup>G. Srinivasan and M. S. Seehra, Phys. Rev. B **28**, 6542 (1983).  
<sup>13</sup>K. H. Germann, K. Maier, and E. Strauss, Solid State Commun. **14**, 1309 (1974).  
<sup>14</sup>C. F. Van Doorn and P. de V. Duplessis, Phys. Lett. **66A**, 141 (1978).  
<sup>15</sup>I. Negovetić and J. Konstantinović, Solid State Commun. **13**, 249 (1973).  
<sup>16</sup>M. Massot, A. Oleaga, A. Salazar, D. Prabhakaran, M. Martin, P. Berthet, and G. Dhahenne, Phys. Rev. B **77**, 134438 (2008).  
<sup>17</sup>M. B. Salamon, Phys. Rev. B **2**, 214 (1970).  
<sup>18</sup>M. D. Rechten, S. C. Moss, and B. L. Averbach, Phys. Rev. Lett. **24**, 1485 (1970).  
<sup>19</sup>K. H. Germann, K. Maier, and E. Strauss, Phys. Status Solidi B **61**, 449 (1974).  
<sup>20</sup>P. S. Silinsky and M. S. Seehra, Phys. Rev. B **24**, 419 (1981).  
<sup>21</sup>C. Glorieux, J. Caerels, and J. Thoen, J. Phys. IV Colloq. **C7-4**, 267 (1994).  
<sup>22</sup>J. Caerels, B. Maesen, and J. Thoen, Prog. Nat. Sci. **6**, S-254 (1996).  
<sup>23</sup>F. J. Romero, J. Jiménez, and J. Del Cerro, J. Magn. Magn. Mater. **280**, 257 (2004).  
<sup>24</sup>M. Chirtoc, D. Dadarlat, D. Bicanic, J. S. Antoniow, and M. Egée, in *Progress in Photothermal and Photoacoustic Science and Technology*, edited by A. Mandelis and P. Hess (SPIE, Bellingham, Washington, 1997), Vol. 3.  
<sup>25</sup>M. Marinelli, U. Zammit, F. Mercuri, and R. Pizzoferrato, J. Appl. Phys. **72**, 1096 (1992).  
<sup>26</sup>D. Dadarlat, V. Surducun, K. J. Riezebos, and D. Bicanic, Instrum. Sci. Technol. **26**, 125 (1998).  
<sup>27</sup>S. Delenclos, A. H. Sahraoui, J. M. Buisine, M. Benmouna, C. Kolinsky, and U. Maschke, Mol. Cryst. Liq. Cryst. **410**, 691 (2004).  
<sup>28</sup>M. Marinelli, F. Mercuri, U. Zammit, R. Pizzoferrato, F. Scudieri, and D. Dadarlat, Phys. Rev. B **49**, 9523 (1994).  
<sup>29</sup>M. Marinelli, F. Mercuri, and D. P. Belanger, Phys. Rev. B **51**, 8897 (1995).  
<sup>30</sup>M. Marinelli, F. Mercuri, S. Foglietta, and D. P. Belanger, Phys. Rev. B **54**, 4087 (1996).  
<sup>31</sup>M. Marinelli, F. Mercuri, U. Zammit, and F. Scudieri, Phys. Rev. E **53**, 701 (1996).  
<sup>32</sup>A. Salazar, M. Massot, A. Oleaga, A. Pawlak, and W. Schranz, Phys. Rev. B **75**, 224428 (2007).  
<sup>33</sup>A. Oleaga, A. Salazar, D. Prabhakaran, and A. T. Boothroyd, Phys. Rev. B **70**, 184402 (2004).  
<sup>34</sup>A. Oleaga, A. Salazar, M. Massot, and Yu. M. Vysochanskii, Thermochim. Acta **459**, 73 (2007).  
<sup>35</sup>C. W. Garland, in *Liquid Crystals: Physical Properties and Phase Transitions*, edited by S. Kumar (Cambridge University Press, Cambridge, England, 2001), Chap. 7.  
<sup>36</sup>F. Mercuri, S. Paoloni, U. Zammit, F. Scudieri, and M. Marinelli, Phys. Rev. E **74**, 041707 (2006).  
<sup>37</sup>F. Mercuri, M. Marinelli, S. Paoloni, U. Zammit, and F. Scudieri, Appl. Phys. Lett. **92**, 251911 (2008).  
<sup>38</sup>P. Saint-Gregoire, R. Almairac, J. Lapsset, and J. Moret, Phys. Status Solidi A **120**, K25 (1990).