Dynamic heat flux experiments in $Cu_{67.64}Zn_{16.71}Al_{15.65}$: Separating the time scales of fast and ultra-slow kinetic processes in martensitic transformations

F. J. Romero,[1,a)] J. Manchado,[1] J. M. Martín-Olalla,[1] M. C. Gallardo,[1] and E. K. H. Salje[2]
[1]*Departamento de Física de la Materia Condensada, Instituto Mixto de Ciencia de Materiales CSIC-Universidad de Sevilla, P.O. Box 1065, E41080 Sevilla, Spain*
[2]*Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, United Kingdom*

(Received 28 April 2011; accepted 15 June 2011; published online 7 July 2011)

Crackling noise and avalanches during the martensite phase transformation of $Cu_{67.64}Zn_{16.71}Al_{15.65}$ were investigated. Heat flux measurements with extremely slow heating rates of 0.005 Kh^{-1} allowed sufficient separation between the continuous background and the avalanche jerks. The jerk enthalpy is below 3% of the total transformation enthalpy. The crackling noise follows power law behavior with an energy exponent near $\varepsilon = 1.8$. The jerks are almost uncorrelated with approximately a Poisson distribution of the waiting times between jerks. Quantitative analysis showed a scaling behavior with $p(wt) \sim wt^{(\gamma-1)}\exp(-wt/\tau)^n$ with $\gamma = 0.7$ and $n \approx 1$. © *2011 American Institute of Physics*. [doi:10.1063/1.3609239]

With increasing miniaturization of devices the problem of noise becomes one of the determinate for their application. With fewer active switching movements in ferroelastic and multi-ferroic devices each noise event can lead to a catastrophic failure of the device. Understanding noise and the formation of defects[1] is crucial for the application of such devices, and some surprising results have already been found: crackling noise is related to the progression of domain boundaries[2–7] but it is not a unique excitation. Additional smooth front propagation can exist, and we will show in this Letter that the largest part of the transformation enthalpy in a martensitic material is related to smooth transitions. Computer simulation has also shown that crackling noise is not necessarily athermal[8,9] and not related to extrinsic defects: intersections between domain boundaries can act as intrinsic defects and nucleate avalanches in the same way as extrinsic defects would do.[10] Experimentally, it is very hard to measure both contributions, namely avalanches and smooth front propagation, simultaneously. Gallardo *et al.*[11] argued that only a few percent of the noise is actually related to avalanches. In this paper we will quantify this observation; we find that less than 3% of the excess enthalpy is due to jerky avalanches while 97% relates to smooth front propagation. The conditions for the distinction between the two contributions lie in a reliable separation of length and time scales. Heat flux measurements during first order phase transitions are very sensitive and register all energy contributions, provided that such measurements are performed slowly enough so that they can separate the relevant time scales.

The coexistence of widely separated time scales of transition processes in martensitic phase transformation was first demonstrated[11] for the Fm3m–I2/m transition in $Cu_{67.64}Zn_{16.71}Al_{15.65}$. To observe these two time scales the temperatures inside the coexistence interval must be scanned with very slow rates so that the avalanches do not overlap. Previous scanning rates of typically 0.29 Kh^{-1} meant that the transformation between the austenite and the martensite phase between 225 and 255 K took some 100 h to complete. This temperature rate was just sufficient to observe the two time scales, but even slower rates are needed to quantify the dynamic behavior. This is a very tall task for experimentalists. We will report in this paper the experimental results with extreme slow rates (0.005 Kh^{-1}), which clarify the previously identified picture of the transition. Such slow measurements of the heat flux of the martensitic phase transition in $Cu_{67.64}Zn_{16.71}Al_{15.65}$ between 235 and 255 K take about 4000 h to measure the complete transition. Our experiments constitute a completely different way to look at discontinuous phase transitions, where previously the latent heat was measured as one quantity; we show here that under extremely slow scanning rates the various fast and slow components of the latent heat can be separated and the physical processes can be identified which lead to the transition process.

Our work was stimulated by recent computer simulations of martensitic shear transformations which show, for low defect concentrations, the typical separation of length and time scales. While phase fronts propagate smoothly with the propagation of kinks in interfaces or as solitary waves,[10] the interaction between twin walls in the martensitic phase generates intersections which act as defects for the propagating interfaces. Their pinning and depinning generates jerks and hence spikes in the total energy. Other previous experimental observations[12–16] include stress induced transformation and the noise of propagating needle domains in $LaAlO_3$. Global statistics were previously observed by acoustic emission (AE) measurements[14] in martensites, and similar mechanisms were found in ferroelastic materials.[17,18]

The sample of $Cu_{67.64}Zn_{16.71}Al_{15.65}$ was described together with the measurement procedure of the heat flux and the specific heat in Ref. 11. We reduced the rate of the temperature change and increased the number of data points which were recorded from 2 to 125 measurements per 10 s. The previous rate of 0.29 Kh^{-1} was already much slower than that usually undertaken in heat flux measurements, we

a)Electronic mail: fjromero@us.es.

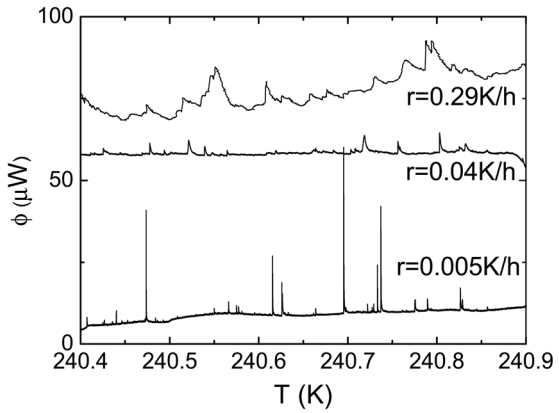

FIG. 1. Jerks of the phase transformation are shown over a small temperature interval of 0.5 K for three scanning rates. Avalanches are shown as jerks while the front propagation constitute a continuous background. With increasingly slower scanning rates the individual avalanches become well resolved.

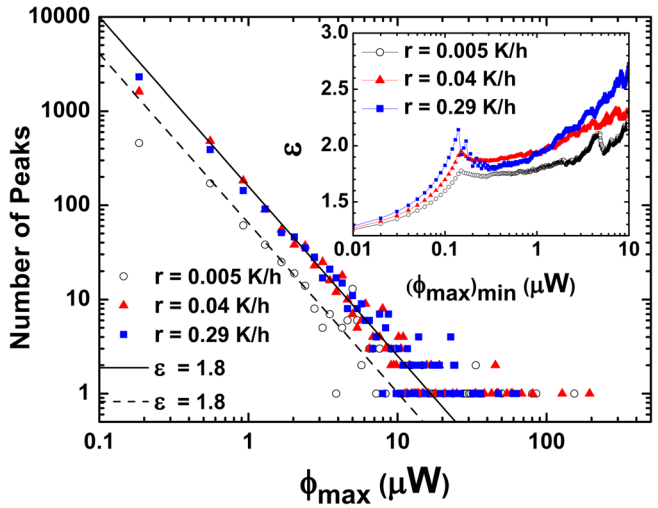

FIG. 2. (Color online) Power law dependence of the jerk energy and its statistical analysis in the maximum likelihood method (inset). The inset shows plateaus at the most reliable exponents near $\varepsilon = 1.8 \pm 0.1$.

now reduced the rate to much lower values which has never been attempted before.

The temperature dependence of the heat flux ϕ is shown for three rates r in Fig. 1. While the individual jerks are visible for all scanning rates, the identification of individual peaks requires rates as low as 0.04 Kh^{-1} (Fig. 1(middle)) and 0.005 Kh^{-1} (Fig. 1(bottom)). Attempts to lower the rate even more found, over short periods of time, peaks at rates as low as 0.001 Kh^{-1}, which is five times lower than the slowest rate reported in Ref. 11.

The jerks were analyzed statistically. The continuous background was stripped from the data in Fig. 1 with the peak heights proportional[11] to the energy per jerk E. Their probability is given by

$$p(E)dE = \frac{E^{-\varepsilon}dE}{\int E^{-\varepsilon}\mathrm{d}E}, \tag{1}$$

where the integration covers the full energy range. The lowest accessible energy per jerk is 1.5×10^{-5} J (corresponding to 150 nW taking into account the characteristic time of the experimental system). The dependence of the apparent exponent ε on the integration rate was analyzed using the maximum likelihood (ML) method (details in Ref. 11) and was found to be very stable, the resulting power law and the ML fits are shown in Fig. 2. The exponent is $\varepsilon = 1.8 \pm 0.1$ which is slightly lower than the previous result in Ref. 11. This value agrees within experimental errors with the results of AE measurements[11,14] which lead to $\varepsilon = 1.8 \pm 0.3$.

The experimental results, which we report in this paper, are the first thermodynamic measurements with sufficient time resolution to distinguish between the individual avalanche contributions or jerks. These jerks are related to avalanches or any other kinetic process which involves the stepwise propagation of the austenite. The maximum number of jerks is near 50% of the transformation with a maximum number of interfaces between martensite and austenite. All jerks follow the same power law distribution which can be determined if the time scale of the experiment is much longer than the waiting time between jerks.

So far, we have discussed the fluxes ϕ as function of rates r. The temperature dependence of ϕ/r is independent of r. The integral of ϕ/r, after appropriate baseline subtraction, leads to the excess enthalpy (Fig. 3). This shows that the excess of enthalpy is indeed independent of r. Here the total enthalpy together with the enthalpy of the jerks is shown. The jerk enthalpy (Fig. 3(inset)) is <3% of the total and restricted to a small temperature interval between 238 and 255 K. The enthalpy of the transition is 370 ± 10 $Jmol^{-1}$ and extends over a wide interval from 215 to 255 K.

We finally explore the intercorrelation of jerks. The waiting time wt between uncorrelated jerks are expected to follow Poisson statistics and display a density function $p(wt) \sim \exp(-wt/\tau)$, any correlations are typically parametrized by

$$p(wt) \sim wt^{-(\gamma-1)} exp(-wt/\tau)^n, \tag{2}$$

where γ and n are the characteristic coefficients while wt is understood to be normalized with the characteristic time scale (if experiments at different time scales are involved). Only measurements with low enough rate separate the jerks

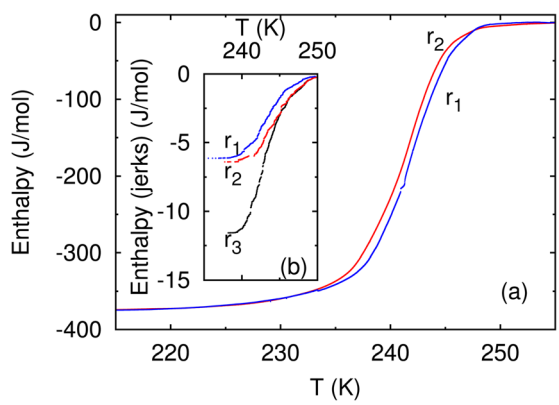

FIG. 3. (Color online) Total enthalpy (a) of the transformation process and jerk-related enthalpy (b). The jerk enthalpy at the faster rates $r_1 = 0.04$ Kh^{-1} and $r_2 = 0.29$ Kh^{-1} are virtually identical. The slowest run ($r_3 = 0.001 - 0.07$ Kh^{-1}) had stops in its time evolution and showed a slightly larger jerk enthalpy.

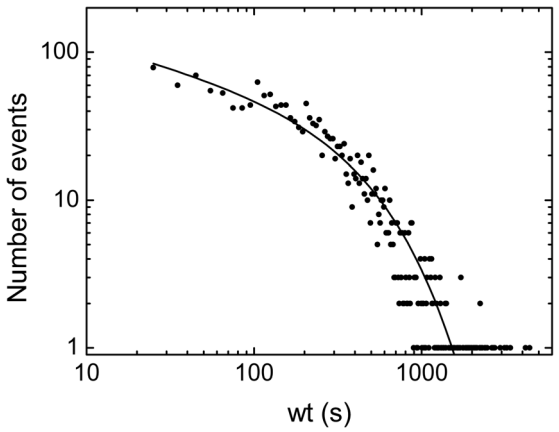

FIG. 4. Statistical distribution of the waiting time between jerks. The quantitative parameterization of the distribution at $p(wt) \sim wt^{-(\gamma-1)}\exp(-wt/\tau)^n$ leads to $n=1$, $\gamma=0.7$, and $\tau=460$ s.

sufficiently to measure the waiting time with the required accuracy (Fig. 1). The statistical analysis shows indeed that most data collapse on an exponential $p(wt)$. The coefficients are, within experimental resolution, $n=1$ and $\gamma=0.7$ (Fig. 4).

The calorimetric experiments have been supported in Seville by Project FIS2006-04045. J. Manchado wishes to thank to Fundación Cámara for a research grant. We want to thank also to Dr. A. Planes for supplying the sample.

[1]C. Ederer and N. A. Spaldin, Phys. Rev. B **71**, 224103 (2005); A. Travesset, R. A. White, and K. A. Dahmen, ibid. **66**, 024430 (2002); S. Conti, S. Müller, A. Poliakovsky, and E. K. H. Salje, J. Phys.: Condens. Matter **23**, 142203 (2011); W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13 (2007).
[2]K. D. J. P. Sethna and C. Myers, Nature **410**, 242 (2001); M. Paczuski, S. Maslov, and P. Bak, Phys. Rev. E **53**, 414 (1996).
[3]R. J. Harrison and E. K. H. Salje, Appl. Phys. Lett. **97**, 021907 (2010).
[4]E. K. H. Salje, J. Koppensteiner, M. Reinecker, W. Schranz, and A. Planes, Appl. Phys. Lett. **95**, 231908 (2009).
[5]R. J. Harrison, S. A. T. Redfern, and E. K. H. Salje, Phys. Rev. B **69**, 144101 (2004).
[6]E. Salje and W. Schranz, Zeitschrift für Kristallographie **226**, 1 (2011).
[7]E. Salje and K. Parlinski, Supercond. Sci. Technol. **4**, 93 (1991).
[8]S. Rao, D. Dimiduk, T. Parthasarathy, M. Uchic, M. Tang, and C. Woodward, Acta Mater. **56**, 3245 (2008).
[9]F. J. Pérez-Reche, E. Vives, L. Mañosa, and A. Planes, Phys. Rev. Lett. **87**, 195701 (2001); X. Illa, M.-L. Rosinberg, and E. Vives, Phys. Rev. B **74**, 224403 (2006).
[10]E. K. H. Salje, X. Ding, Z. Zhao, T. Lookman, and A. Saxena, Phys. Rev. B **83**, 104109 (2011).
[11]M. C. Gallardo, J. Manchado, F. J. Romero, J. del Cerro, E. K. H. Salje, A. Planes, E. Vives, R. Romero, and M. Stipcich, Phys. Rev. B **81**, 174102 (2010).
[12]A. Clauset, C. R. Shalizi, and M. E. J. Newman, SIAM Rev. **51**, 661 (2009).
[13]F.-J. Pérez-Reche, B. Tadić, L. Mañosa, A. Planes, and E. Vives, Phys. Rev. Lett. **93**, 195701 (2004).
[14]A. Planes, J. L. Macqueron, M. Morin, and G. Guenin, Phys. Status Solidi A **66**, 717 (1981).
[15]E. Vives, J. Ortín, L. Mañosa, I. Ráfols, R. Pérez-Magrané, and A. Planes, Phys. Rev. Lett. **72**, 1694 (1994).
[16]T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, A. Planes, E. Suard, and B. Ouladdiaf, Phys. Rev. B **75**, 104414 (2007).
[17]U. Bismayer and E. Salje, Acta Crystallogr. Sect. A **37**, 145 (1981); E. K. H. Salje, A. Graeme-Barber, M. A. Carpenter, and U. Bismayer, Acta Crystallogr. Sect. B **49**, 387 (1993).
[18]E. Salje and B. Wruck, Phys. Rev. B **28**, 6510 (1983).