

gas did not have any effect on  $T_c$ , as the boiling point of  $O_2$  is higher than the  $T_c$  of our sample.

D.D. SARMA  
C.T. SIMMONS  
G. KÄINDL

Fachbereich Physik,  
Freie Universität Berlin,  
D-1000 Berlin 33, FRG

I. Matthews, D.N., Bailey, A., Vaile, R.A., Russell, G.J. & Taylor, K.N.R. *Nature* 328, 786-787 (1987).

MATTHEWS *et al.* reply—The mechanism suggested by Sarma *et al.* was rejected at an early stage in our studies. Simple calculation shows that the heat flow from the outside of a sample maintained at 93 K, say, by exchange gas, to a core of liquid nitrogen at 77 K in the centre of the sample is relatively rapid for the samples used in our studies, which are typically 1–2 cm long and  $2 \times 1$  mm in cross-section. This heat flow will totally vaporize any stored liquid nitrogen within a few seconds, assuming a thermal conductivity value of  $4 \text{ W m}^{-1} \text{ K}^{-1}$  (ref. 1). Consequently, at the heating rates of  $0.3 \text{ K min}^{-1}$  used by ourselves<sup>2</sup>, equilibrium is maintained throughout the experiment.

The information provided by these authors is inadequate to allow us to estimate the thermal time constant in their case. However, we did carry out an experiment similar to that detailed in their Fig. 2 as part of our original attempts to understand the role played by nitrogen in enhancing  $T_c$ . We observed that a stay of 30 min in vacuum, after nitrogen treatment, in the temperature range from ( $T_c - 24$  K) to  $T_c$ , did not affect the enhanced value of  $T_c$  (120.5 K) in that experiment. This result is extremely important in that it suggests that the increase in  $T_c$  is stable against chamber evacuation provided that  $T < 120$  K. It also confirms that if any liquid nitrogen condenses within the pores of the sample it is rapidly vaporized and remains in thermal equilibrium with the sample for all temperatures at the heating rate used in this case ( $\sim 1 \text{ K min}^{-1}$ ).

Further evidence for the nature of this enhancement effect comes from a recent careful study of the increase in  $T_c$  caused by the controlled addition of nitrogen. As shown in Fig. 1, the continuous exposure of low-density samples to nitrogen leads to a sequence of forms of the  $R(T)$  behaviour near to the transition, where  $R$  is resistance and  $T$  temperature. A model involving the vaporization of stored liquid nitrogen would lead only to changes in  $T_c$  and would leave the shape of  $R(T)$  at the transition unaltered.

Further evidence, which has been obtained consistently, is the improvement of the critical current/critical field behaviour as nitrogen is absorbed into the specimen<sup>3</sup>. Such changes are clearly not consistent with the model proposed.

As the specimen dimensions would

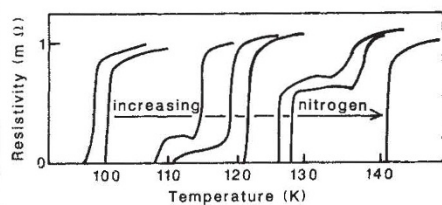


Fig. 1 The resistive transition at various stages in the establishment of a 141-K transition temperature by controlled absorption of nitrogen gas into the sample at low temperatures.

have a direct effect on the vaporization time, and therefore on the observed  $T_c$ , if the system were not in equilibrium owing to liquid nitrogen stored in the core, we have made identical observations on two specimens cut from the same sample but with cross-sectional dimensions ( $r$ ) differing by factors of  $\sim 3$  (corresponding to a factor of nine change in cross-sectional area). Both samples showed identical critical temperatures and  $R(r)$  variations both before ( $T_c = 90$  K) and after nitrogen treatment ( $T_c = 111$  K). These data also support the view that this effect is not the result of an artefact of the type envisaged by Sarma *et al.*

Despite this weight of evidence, during the past few days we have also carried out a direct measurement of the temperature difference existing in our samples during heating and cooling, using thermocouples

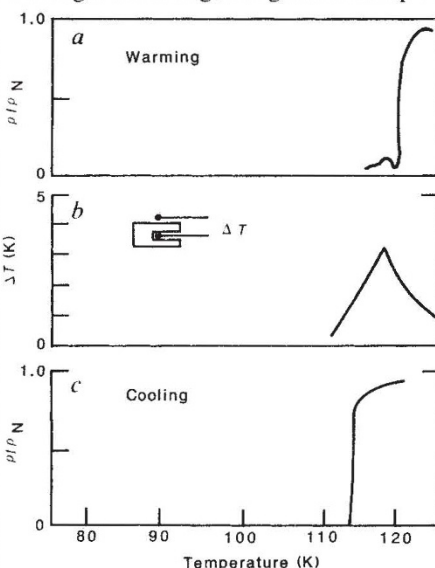


Fig. 2 Changes in internal temperature gradient ( $\Delta T \equiv T_{\text{surface}} - T_{\text{core}}$ ) with temperature during warming and cooling through a nitrogen-enhanced transition. In the warming cycle (a),  $T_c = 113$  K, and an onset structure appears near  $T_c$ ; on cooling (c),  $T_c$  is reduced by 5 K, and there is no structure below  $T_c$ .  $\Delta T$  was  $< 0.2$  K at all times during cooling. The structure observed during warming at temperatures below the main transition is associated with a Seebeck voltage which appears along the sample, owing to a small temperature gradient parallel to the current direction. The magnitude of this temperature gradient varies with temperature in the same way as the observed transverse  $\Delta T$  shown in b.

embedded in the superconductor, and correlated these with the electrical properties measured simultaneously. Figure 2 shows the change in  $R$  and  $\Delta T$  ( $\equiv T_{\text{surface}} - T_{\text{core}}$ ) with temperature during a heating and cooling study of the transition. As may be seen (Fig. 2b), a temperature lag ( $\Delta T$ ) of  $\sim 3$  K appears close to the resistive onset at  $T_c$  during warming. This lag begins at a few degrees below  $T_c$  and peaks just above  $T_c$ . The major resistive transition (Fig. 2a) occurs just after the peak in  $\Delta T$ . On cooling (Fig. 2c) there is only a single transition at  $T_c$ ; that is, there is hysteresis of  $\sim 5$  K in the major transition. In a similar measurement of helium-treated material, for which there was a single transition at  $T_c = 118$  K, there was again an observable  $\Delta T$  which also reached its peak value just above  $T_c$ . At no time in these experiments did  $\Delta T$  exceed 4.5 K, and thus no evidence exists for liquid nitrogen in the sample core.

Finally, as it appears that we have indeed observed an intrinsic property of these materials, it is appropriate to try to reinterpret the evidence presented by Sarma *et al.* in their Fig. 2. Contact resistances are typically high in these materials and may lie in the range 1–10  $\Omega$ . With a sample current of 10 mA the local heating at the electrodes can be enough to make this region of the sample normal. As the temperature at their measuring point is  $0.93T_c$ , the critical current density  $J_c$  must be relatively small. The combination of electrode heating and the subsequent temperature rise of the sample will eventually drive the sample normal, as observed by Sarma *et al.*

Unfortunately, in the absence of any details of the experimental technique and contact resistances, it is impossible to do more than suggest that their interesting result is indeed the observation of a nitrogen-enhanced thermal transition at the elevated temperature, driven by the self-heating of the electrodes, combined with effects associated with the critical current density.

K.N.R. TAYLOR  
G.J. RUSSELL  
D.N. MATTHEWS  
A. BAILEY

Advanced Electronic Materials  
Technology Group,  
School of Physics,  
University of New South Wales,  
PO Box 1, Kensington, NSW 2033,  
Australia

R.A. VAILE  
School of Business Technology,  
Macarthur Institute of Higher Education,  
PO Box 108, Milperra, NSW 2214,  
Australia

1. Uher, C. & Kaiser, A.B. *Phys. Rev.* B36(10), (1987).
2. Matthews, D.N., Bailey, A., Vaile, R.A., Russell, G.J. & Taylor, K.N.R. *Nature* 328, 786-787 (1987).
3. Taylor, K.N.R. *et al.* *Phys. Rev.* B (submitted).