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LETTER TO THE EDITOR

The possibility of an above-room-temperature superconducting phase in xCuBr.CuBr$_2$

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Abstract. Electrical transport properties of xCuBr.CuBr$_2$ are investigated. Evidence suggesting the occurrence of a superconducting phase in this material with a mid-point transition temperature of 346 K (73 °C) is presented.

Since the discovery of high-temperature superconductivity in rare-earth–copper oxides [1–4], many workers world-wide have engaged in the search for materials with even higher critical temperatures [5–11]. Most of the experiments in this direction are based on attempts to demonstrate the existence of phases with higher T_c in the rare-earth–copper oxide system or its modifications [5–11]. Finding a non-oxide high-T_c material would provide an impetus for practical and theoretical developments in this field. Some time ago there was a suggestion that the anomalies observed in cuprous chloride [12, 13] are associated with high-T_c superconductivity [14, 15]. Motivated by these reports, we conducted a systematic examination of cuprous halides and found evidence suggesting a superconducting phase in xCuBr.CuBr$_2$, with a mid-point transition temperature as high as 346 K (73 °C).

CuBr was prepared by digestion of pure copper in a hot de-aerated solution of CuBr$_2$ acidified with HBr. Cu(I) bromide which precipitates on dilution was separated and washed with alcohol. Cu(I) and Cu(II) bromides were ground together in an agate mortar and dried in vacuum at 40 °C for several hours to remove moisture. The powder was compacted between gold-studded copper electrodes in a Pyrex tube (diameter $\simeq 0.45$ cm, pellet length $\simeq 0.8$ cm) to a pressure of about 0.35 kbar and the ends were sealed with epoxy resin. Pt wires (separation $\simeq 4$ mm) inserted through the glass served as the voltage terminals in the four-probe resistance measurement (inset, figure 1). Pure CuBr which crystallises in the zincblende structure is a semiconductor, $\sigma(26\,°C) \simeq 7 \times 10^{-8}\,\Omega^{-1}\,cm^{-1}$. Doping with CuBr$_2$ was found to increase the conductivity drastically and an optimum of $9 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at 26 °C is reached when $x \simeq 19.4$ (figure 1). The temperature variation of σ at this composition is shown in figure 2. A transition from a metal-like to a semiconductor phase occurs at 333 K. The voltage gradient (VG) applied to the current leads in the above measurements is $\simeq$2–10 V cm^{-1}. When the VG is increased to about 200 V cm^{-1}, the current passing through the sample gradually

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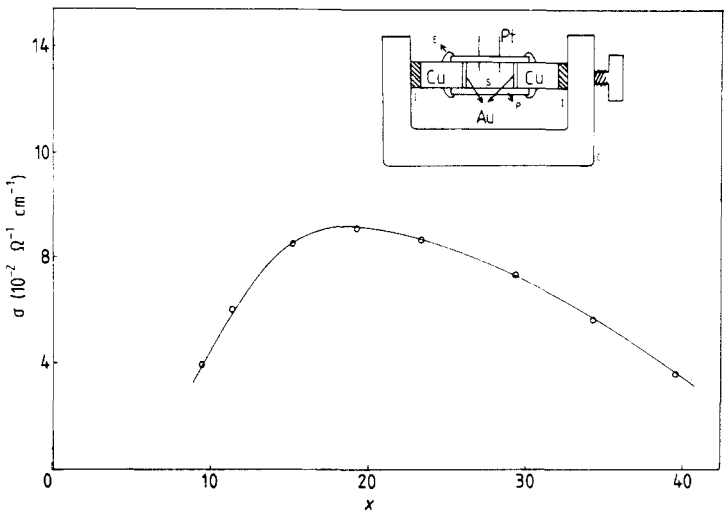

Figure 1. The plot of $\sigma(26\,^{\circ}\mathrm{C})$ versus x before applying the current pulse. Inset is the experimental arrangement (S—sample, P—Pyrex tube, E—epoxy, I—insulator, C—clamp).

increases and reaches a stable saturation in 5–10 min. The associated resistance drop is retained when the current is reduced to an arbitrarily small value. A four-probe measurement (Advantest Digital Electrometer) showed that the resistance had become 'zero' to the limit of resolution of the measurement $\sim 10^{-7}\ \Omega$. On cooling (up to liquid-N_2 temperature), 'zero resistance' is maintained. However, upon heating, a sudden transition to a resistive state begins at $T_c(0) \simeq 329$ K (figure 3); the mid-point of the transition is at 346 K. The same behaviour is reproduced on heating as well as cooling

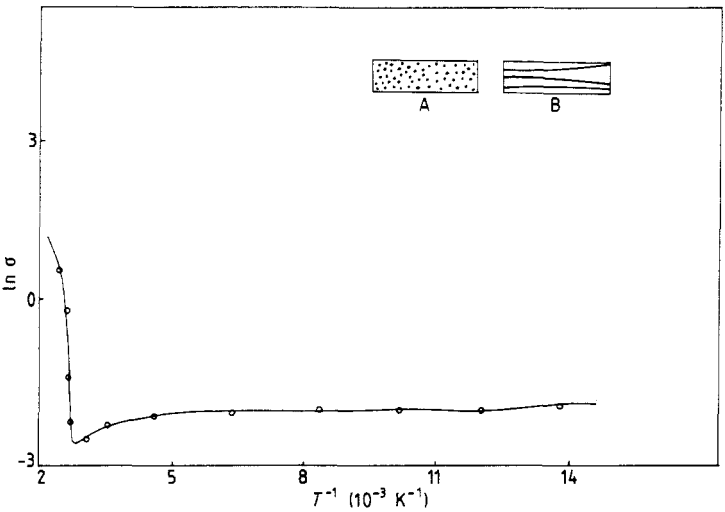

Figure 2. The plot of $\ln(\sigma$ in $\Omega^{-1}\,\mathrm{cm}^{-1})$ versus T^{-1} at optimum x before applying the current pulse. Inset is a schematic diagram showing the distribution of the superconducting (dark) and semiconducting (white) phases (A) before and (B) after the application of the current pulse.

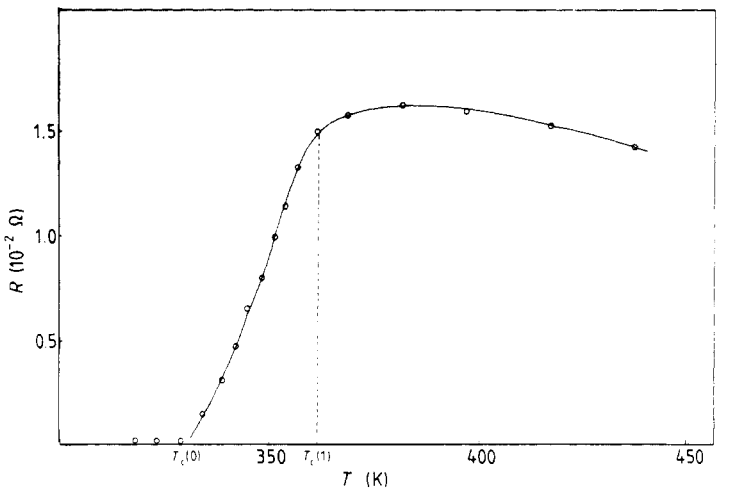

Figure 3. The temperature dependence of resistance after the application of the current pulse.

and survives repeated cycles. The 'superconducting property' induced by a current pulse is not destroyed even if the sample is heated to a temperature of about 50 °C above the T_c for several hours. At room temperature reversions are seen to occur in 2–3 days. To eliminate the uncertainties arising from thermal and contact voltages, *V–I* plots were also examined. Below $T_c(1)$ they fit into lines almost parallel to the *I* axis. At higher current densities ($\geq$125 A cm^{-2}) positive gradients were sometimes noticed. This is more likely to be a result of heating of the contact points of the current leads than an approach of a critical current density. Above $T_c(0)$, *V–I* plots show clear evidence of non-zero resistance.

CuBr and xCuBr.$CuBr_2$ exhibit feeble diamagnetism. We have not succeeded in detecting a magnetic anomaly around the transition temperature. However, low-field

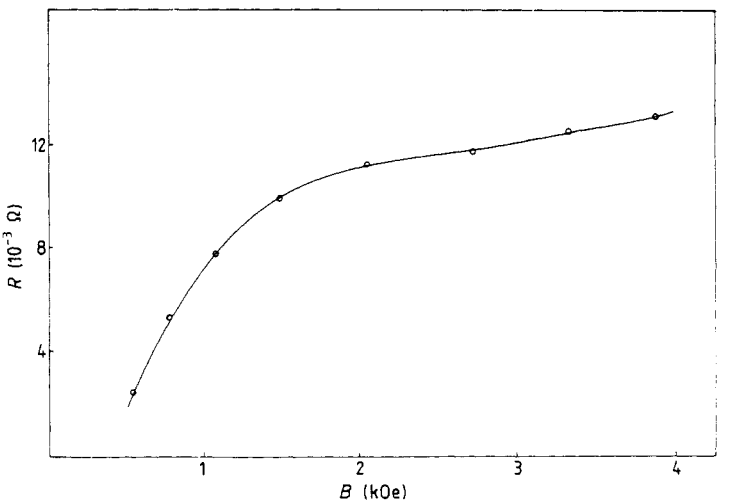

Figure 4. Longitudinal magnetoresistance in the 'superconducting state' (26 °C).

longitudinal magnetoresistance measurements again favour superconductivity. Current-pulsed samples show magnetic field dependence of the resistance characteristic of superconductivity [9] (figure 4). Furthermore, this property is not seen when $T > T_c$.

The above observations can be explained on the assumption that xCuBr.$CuBr_2$ contains a superconducting phase with a T_c above room temperature. Our inability to detect a diamagnetic anomaly is an indication that this phase is only a small fraction of the semiconducting bulk. The passage of the current seems to generate superconducting percolative channels. It is interesting to note that the metal-to-semiconductor-like transition seen before passing the current occurs at a temperature close to $T_c(0)$ (figure 2). Here the superconducting grains are randomly distributed (inset of figure 2). When $T > T_c(1)$, the current-pulsed samples show a slight decrease of resistance with the increase of T. The superconducting phase probably transforms into a metallic phase as T exceeds $T_c(1)$; the observed behaviour could be a combination of the bulk semiconduction and metallic conduction across the percolative paths. The transformation to the 'zero-resistance' state is easiest to achieve when x corresponds to the optimum conductivity. However, the samples where x deviates widely from this value also become 'superconducting' on exposure to stronger VGS. Once transformed, they all have the same $T_c(0)$ irrespective of the value of x. We are unable to think of an alternative other than superconductivity to account for the observations. The possibility that the material in the conducting channels undergoes a transition from one metallic state to another metallic state of high conductivity is most unlikely. In such a situation a detectable resistance should appear on varying x, as a consequence of the change in the fraction of the highly conducting phase. Again on this assumption the observed magnetoresistance cannot be understood. Extreme precautions were taken to rule out possible vanishing of the voltage across the probes due to external factors, e.g., loss of electrical contact as a result of thermal expansion. Current leads were kept clamped to avoid the yielding of the epoxy resin. When different types of glass or plastic were used to encapsulate the pellet, T_c remained identical. All measurements were reproducible and the passage of the current was not found to induce chemical changes. AC (50 Hz) current pulses were equally effective in transforming samples to the 'zero-resistance' state. We have not succeeded in identifying the different phases that could exist in xCuBr.$CuBr_2$. The mechanism of conduction remains unknown. A possibility is the presence of a phase (perhaps at the grain boundaries) where copper occurs in different valence states Cu^0, Cu^+, Cu^{2+} and/or Cu^{3+}. It is also important to understand the mechanism by which a pulse of current generates percolative paths. The differential heating of the resistive and superconducting portions is one possibility. There are indications that even in the Y–Ba–Cu–O system current pulses enhance phase separation [11]. Improvements of the limit of resistance were prevented by the existence of voltage fluctuations and a random-step (parallel to the I axis) type of behaviour in the V–I curves, perhaps originating from the Josephson effect.

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