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Superconductivity in the 100–120 K region in oxides of the Tl-Ca-Ba-Cu-O system⁺

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Abstract. Oxides with different cation ratios 2122, 2212, 2213 and 2223 in the Ti-Ca-Ba-Cu-O system exhibit onset of superconductivity in the 110–125 K range with zero-resistance in the 95–105 K range. Electron microscopic studies show dislocations, layered morphology and other interesting features. These oxides absorb electromagnetic radiation (9·11 GHz) in the superconducting phase.

Keywords. High-temperature superconductivity; $Tl_2CaBa_2Cu_2O_{8+\delta}$; Tl-Ca-Ba-Cu-O system.

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Since the initial discovery of rare-earth-Ba-Cu-O superconductors with T_c's in the range of 90 K, two new families of rare-earth-free cuprate systems have been found to show superconductivity in the range of 100 K. One of these is the Bi-M-Cu-O system where M = alkaline earth metal (Chu *et al* 1988; Rao *et al* 1988; Tarascon *et al* 1988), the other involving thallium. Sheng and Hermann (1988) have shown that $Tl_2Ba_2Cu_3O_{8+\delta}$ has an onset of superconductivity at 90 K with zero-resistance at 81 K. Oxides of the Tl-Ca-Ba-Cu-O system with different ratios of cations have also been discovered with zero-resistance around 100 K and onset around 120 K (Hazen *et al* 1988). We have investigated several oxides of the Tl-Ca-Ba-Cu-O and related systems and report some preliminary results in this communication.

In figure 1a, we show the X-ray diffraction pattern of a sample of $Tl_2CaBa_2Cu_2O_{8+x}$ (2122), prepared from Tl_2CO_3, freshly prepared CaO, BaO_2 and CuO. The mixture was first heated in air for 5 minutes in a preheated furnace at 1170 K and was slowly cooled to room temperature in the furnace. The X-ray diffraction pattern clearly shows a unit cell with a c-parameter of ~ 30 Å. Moreover the X-ray diffraction pattern is similar to that of $Bi_2CaSr_2Cu_2O_{8+\delta}$. In table 1 we give powder X-ray data of the pure 2122 phase. Heating the 2122 phase further (after pelletizing) at 1170 K as above, leads to sharper X-ray lines but also generates some $BaCuO_2$ (figure 1b). We have found the X-ray diffraction patterns of $Tl_2Ca_2BaCu_2O_x$(2212) to be similar to that of the 2122 sample (figure 1c); we see that some $BaCuO_2$ is present in the 2212 sample as well. The X-ray

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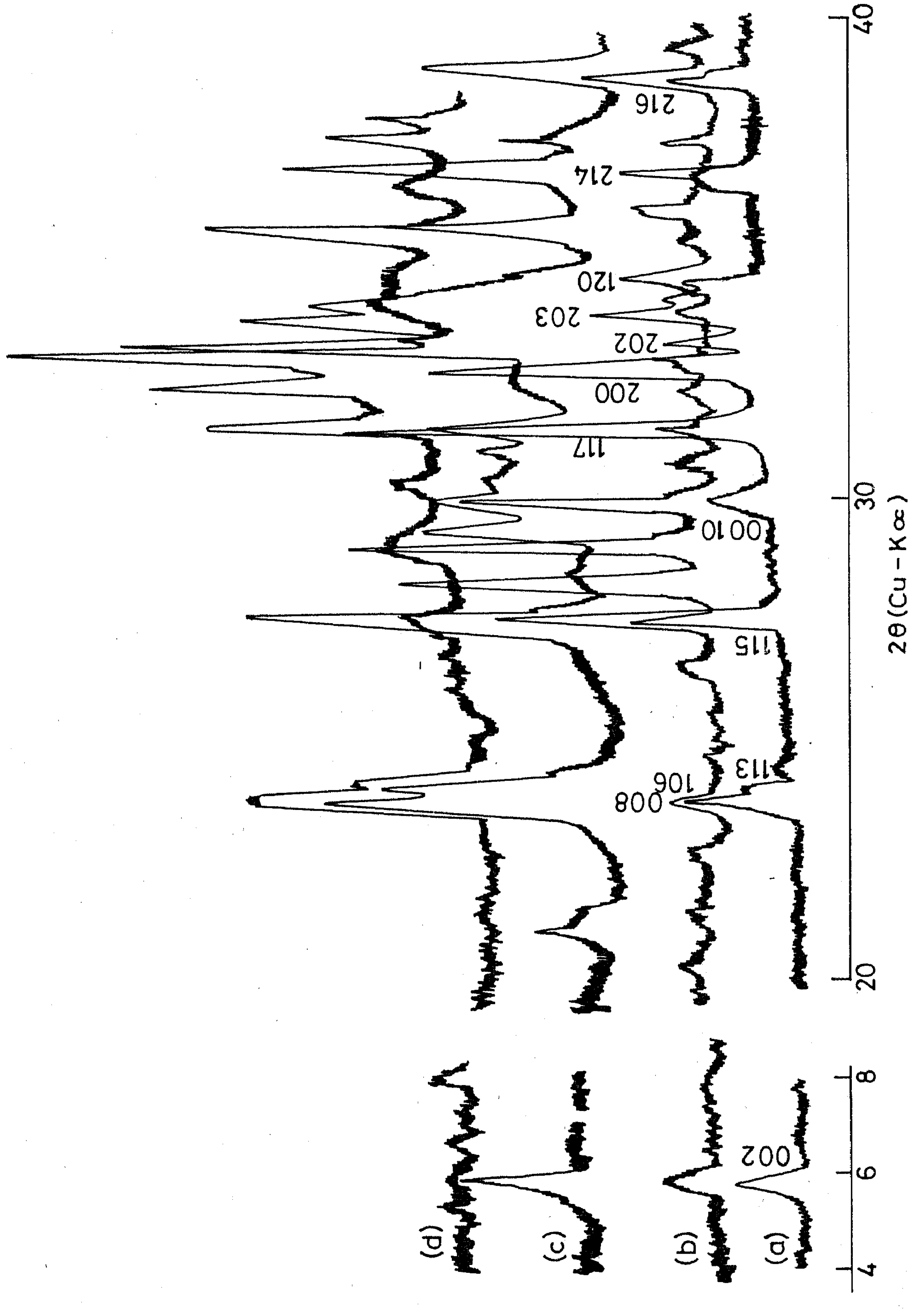

Figure 1. X-ray diffraction patterns of (a) 2122 as prepared, (b) 2122 heated further, (c) 2212 and (d) 2213 members of the Tl-Ca-Ba-Cu-O system.

Table 1. Powder X-ray diffraction data of $Tl_2CaBa_2Cu_2O_x$*.

$h\ k\ l$	d_{obs}(Å)	d_{cal}(Å)	I/I_0
0 0 2	14·979	14·900	10
0 0 4	7·406	7·450	2
0 0 8	3·746	3·725	25
1 0 6	3·700	3·684	15
1 1 3	3·619	3·613	4
1 1 5	3·243	3·251	60
0 0 10	2·980	2·980	15
1 1 7	2·858	2·867	100
2 0 0	2·743	2·740	85
2 0 2	2·698	2·698	15
2 0 3	2·652	2·647	10
—	2·600	—	8
1 2 0	2·455	2·455	20
2 1 4	2·332	2·329	12
2 1 6 }	2·201	2·198	15
2 0 8 }		2·207	
1 1 12	2·103	2·094	10
0 2 10	2·027	2·020	8
2 2 0	1·939	1·940	40
3 0 0	1·829	1·826	25
3 1 5	1·664	1·664	20
2 2 10	1·632	1·626	5
3 1 7 }		1·605	
	1·601		25
1 1 17 }		1·597	
0 0 19	1·576	1·568	10
2 2 12	1·520	1·529	14
2 2 14	1·435	1·429	8
2 0 18 }		1·427	
	1·423		4
0 0 21 }		1·419	
4 0 0	1·372	1·370	8

*Indexed on an orthorhombic cell with $a = 5{\cdot}479$, $b = 5{\cdot}493$ and $c = 29{\cdot}80$ Å.

diffraction pattern of the 2213 sample is shown in figure 1d. This sample also shows the presence of $BaCuO_2$ along with the superconducting phase. We generally find that the most stable phase is pseudo-tetragonal 2122. We have also prepared $Tl_2Ca_2Ba_2Cu_3O_x$ (2223) with $C \simeq 36$ Å; this sample has a tendency to form 2122 and $BaCuO_2$, if the conditions are not perfect. It is most crucial that we avoid evaporation of Tl_2O_3 by heating for a minimum amount of time in a preheated furnace and follow a proper cooling schedule.

We have carried out electron microscopic investigations of these Tl-Ca-Ba-Cu-O oxides. Bright-field images of the 2122 sample show evidence of layered morphology (figure 2) similar to the analogous Bi phase. In figure 3 we show a typical lattice image of the 2122 phase (with 15 Å fringes), the dark bands probably corresponding to the Tl layers. We have found evidence for dislocations in many of these phases, similar to the oxides of the Aurivillius family (Rao and Gopalakrishnan 1986) as well as those of the

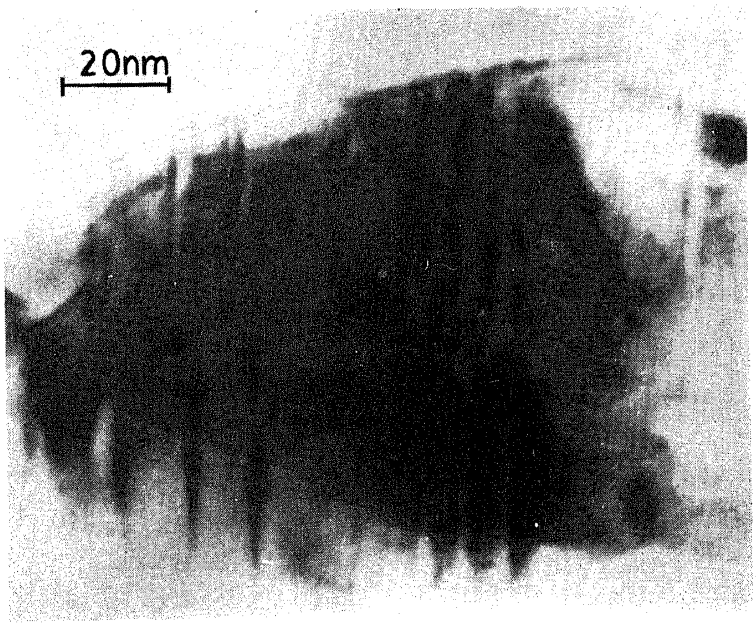

Figure 2. Bright-field image of 2122 suggesting layered morphology.

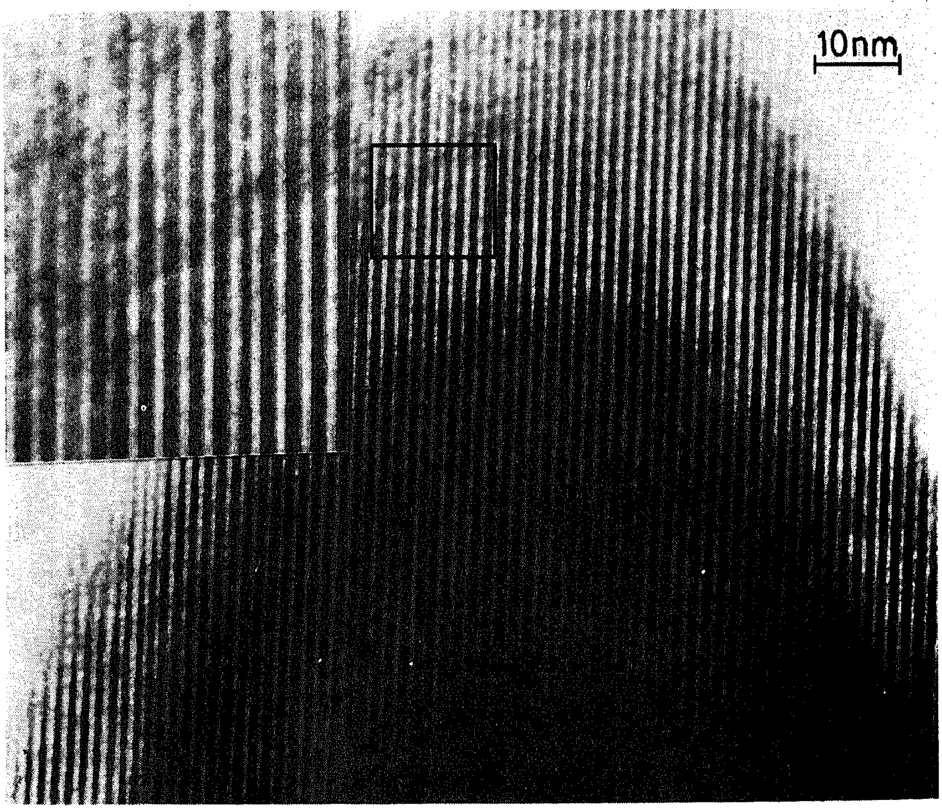

Figure 3. Lattice image of 2122.

Bi-Ca-Sr-Cu-O oxides (Rao *et al* 1988). Some of the crystals also show intergrowths of different layered sequences, associated with a distribution of *c*-parameters. Electron diffraction patterns of 2122 and related oxides correspond to pseudo-tetragonal (or slightly orthorhombic) unit cells.

In figure 4 we show the electrical resistivity data of 2122, 2212, 2213 and 2223 samples of the Tl-Ca-Ba-Cu-O system. All these members show zero-resistance between 95 K and 105 K and onset of superconductivity between 110 and 125 K.

AC susceptibility data of two members are shown in figure 5, we have found large Meissner effect in these samples showing onset of diamagnetism well above 100 K.

We have studied the absorption of electromagnetic radiation by Tl-Ca-Ba-Cu-O high T_c superconductors. The phenomenon of enhanced absorption of electromagnetic

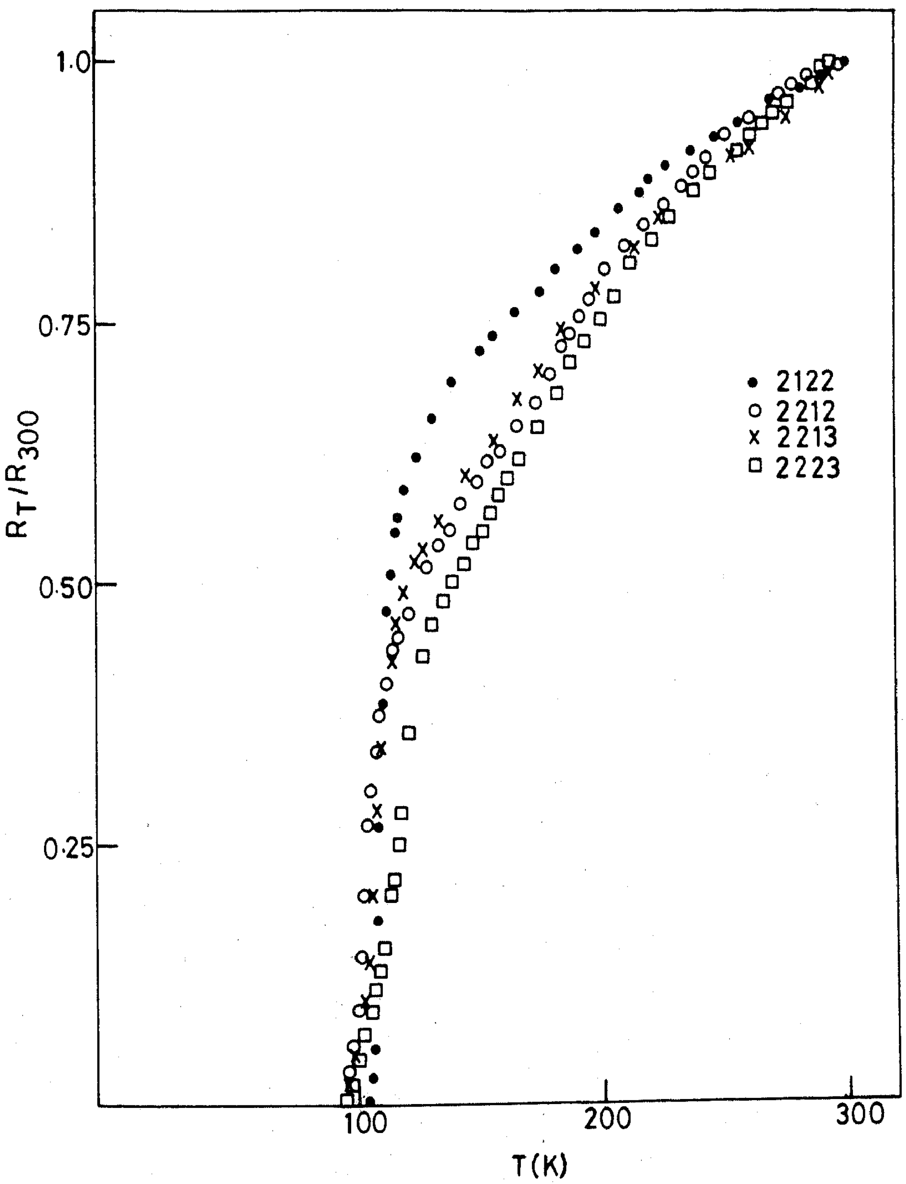

Figure 4. Resistivity behaviour of 2122, 2212, 2213 and 2223 (nom) members of the Tl-Ca-Ba-Cu-O system.

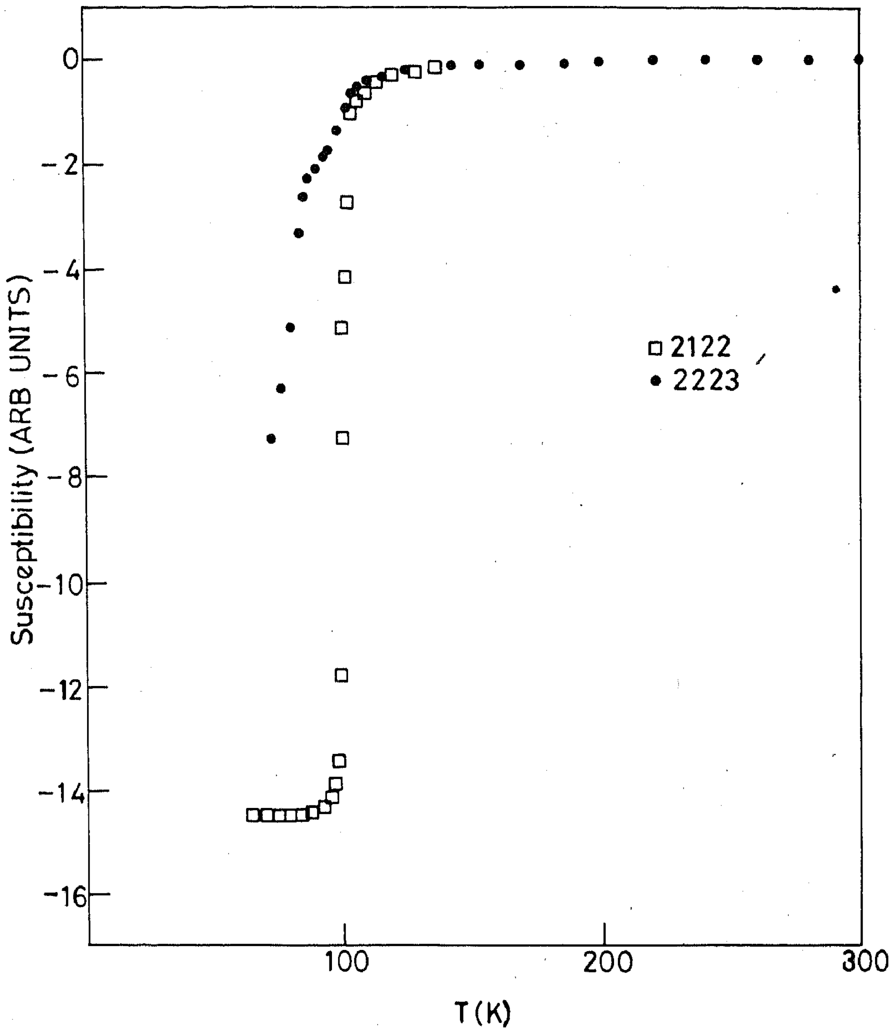

Figure 5. AC susceptibility (Meissner effect) data of 2122 and 2223.

radiation by the high T_c superconducting oxides was first discovered by us (Bhat *et al* 1987a, b) in the case of $YBa_2Cu_3O_7$ and subsequently observed by other workers (see for example Portis *et al* 1988). This phenomenon provides a useful technique for characterizing the samples with respect to their superconducting transition, the critical fields and also the quality of the samples. Figure 6 shows the derivatives of the absorption signals from the 2122 oxide recorded at various temperatures using a conventional x-band EPR spectrometer operating at a frequency of 9·11 GHz. A 100 kHz modulating field of 0·1 G strength was used. The signals below 0 mT were recorded using a pair of current-carrying Helmholtz coils providing an auxiliary magnetic field in a sense opposite to that of the electromagnet. As shown in the figure, the signal appears at T_c, keeps increasing in intensity and width as the temperature is decreased, but retaining the centre at the same value of the field (~ 0 mT) consistent with the non-resonant nature of the phenomenon.

As in the case of our previous report on the $YBa_2Cu_3O_{7-\delta}$ samples (Bhat *et al* 1987a, b), we obtain an enhancement (by about an order of magnitude) of the signal intensity when exposed to the atmosphere (presumably due to the oxygen therein) compared to the samples evacuated to $\sim 0{\cdot}1$ torr. However, it must be mentioned that

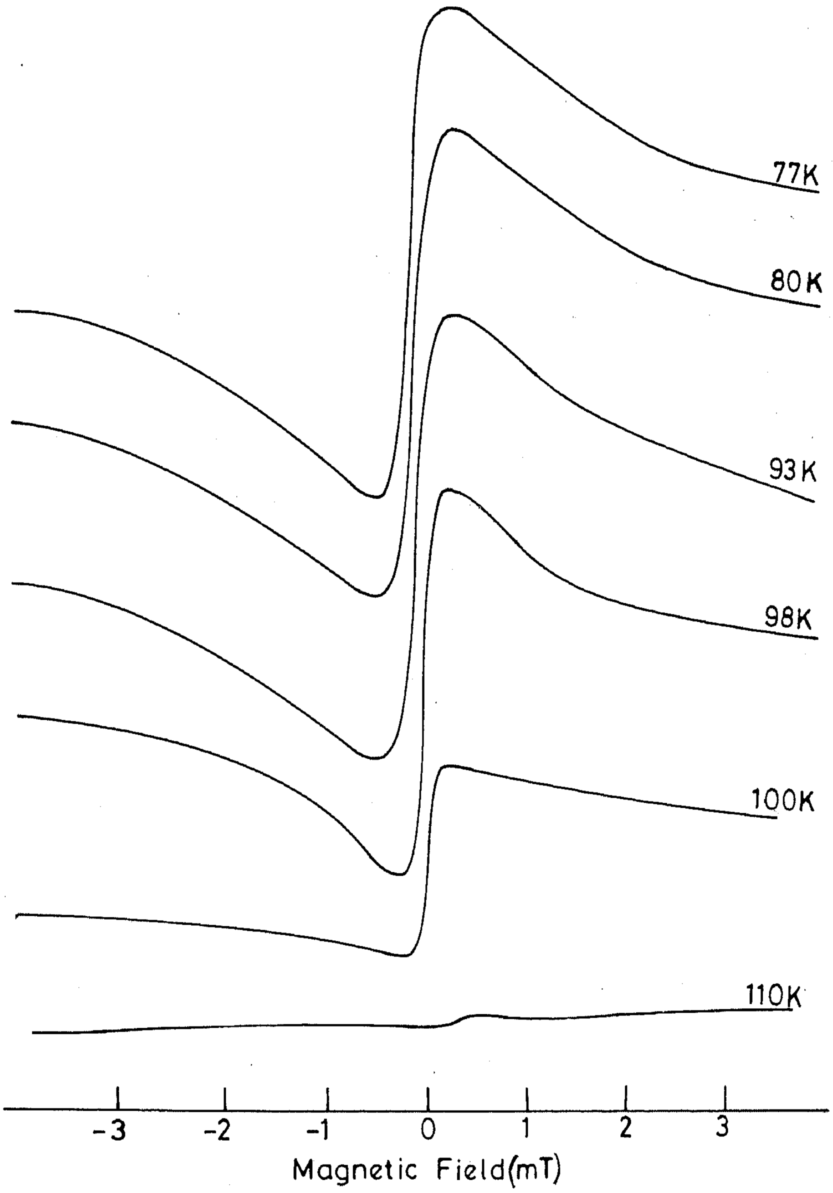

Figure 6. Derivatives of absorption signals of the 2122 oxide at various temperatures recorded at 9·11 GHz.

the actual magnitude of the enhancement depends greatly on the quality and history of the sample. Hysteresis effects were also observed between the forward and the reverse magnetic field sweeps as in the case of the previous studies. There was practically no signal due to Cu^{2+} at $g \approx 2$ indicating the single phase nature of the compound.

We have investigated 2122 and other systems where both Tl and Bi are present and find these oxides also to be superconducting. Thus $TlBiCaBa_2Cu_2O_x$ shows onset of superconductivity around 100 K, but the behaviour is different from Tl-Ca-Ba-Cu-O phases. We are also studying the Tl-Pb-Cu-O system as well as intergrowths, results of which will be published elsewhere.

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