

strong-coupling superconductors Pb and Hg.

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SUPERCONDUCTIVITY IN CERAMIC, MIXED TITANATES*

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We have observed superconductivity in semiconducting specimens of the mixed compounds $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ and $(\text{Ca}_y\text{Sr}_{1-y})\text{TiO}_3$, when $x \leq 0.1$ and $y \leq 0.3$. Some of the insulating compounds are ferroelectrics; reduced specimens are semiconductors. This work was prompted by the recent developments concerning superconductivity in semiconductors.¹⁻³ Cohen's theoretical treatment⁴ indicates that the occurrence of superconductivity depends on a strong electron-phonon interaction; both the effective mass m^* of the charge carriers and the dielectric function $\epsilon(\omega, q)$ play an important role. The latter function contains the static dielectric constant ϵ_0 of the lattice (without electrons).

In order to investigate the effect of these parameters on the superconducting transition temperature T_c , it is desirable to change the symmetry or the lattice parameter of the solid. This can be achieved either by pressure (uniaxial or hydrostatic) or by substitution. Replacement of the Sr ion in SrTiO_3 by Ba or Ca gives rise to small, but gradual, changes in the lattice constant^{4,5}; at the same time the static dielectric constant ϵ_0 is drastically modified.^{4,6,7}

Previous work of this laboratory concerned with the semiconductivity and superconductivity of reduced SrTiO_3 has been performed on single crystals of the compound.^{8,9} We realized that studies of the systems $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ and $(\text{Ca}_y\text{Sr}_{1-y})\text{TiO}_3$ would be greatly facilitated if ceramic samples could be used. Initial measurements on reduced ceramic specimens of pure SrTiO_3 indicated superconductivity at transition temperatures about equal to those of single crystals of the same carrier concentration.^{9,10} Encouraged by this result, we decided to use only ceramic samples in this study of mixed titanates.

Samples were prepared by pressing and were then subjected to a final sintering at $\sim 1650^\circ\text{C}$. The high sintering temperature is necessary to produce grains larger than the penetration depth.¹¹ Samples containing 0-20% Ba and 0-100% Ca were prepared and reduced in hydrogen. The Ba and Ca content was checked by determining the lattice parameter^{4,5} from x-ray measurements. The substituted amounts deduced from these experiments are shown in Table I beside the nominal values. The composition appeared to be quite homogeneous

throughout the specimens.

The electron concentrations n (Table I, column 4) of our samples were deduced from the Hall-effect determinations at liquid-helium temperatures. The Hall coefficient is constant in this temperature range. The concentration n is $(6 \pm 3) \times 10^{19} \text{ cm}^{-3}$ for all mixed titanate samples (excluding samples CHR7 and CHR11). Consequently, a comparison of the transition temperatures of these specimens may be possible in spite of the fact that T_c is concentration dependent.⁹

The superconductivity of some 20 samples was tested in two different ways. In the first method^{3,9} the ac susceptibility was measured as a function of temperature between 0.10 and 1.0°K. The transition usually stretched over a considerable range of temperature, presumably because of the large penetration depth and the variation in grain size. T_{cH} (Table I) is taken from the foot of the χ -vs- T curves at the high-temperature side.

The transition temperatures of several samples were determined also from a series of magnetization curves at different temperatures.

Table I. Characteristics, superconducting transition temperatures, and critical fields of mixed titanates.

Sample	Percentage Ba or Ca		n ($10^{19}/\text{cc}$)	T_{cH} (°K)	T_{cVM} (°K)	\bar{H}_{c1} (Oe)
	nominal	from lattice constant				
CHR4	0		5.4	0.37		
CHR13	0		5.8	0.23	0.30	2.7
CHR19	0		6.4	0.30	0.28	2.75
CHR27	0		1.7	0.12		
CHR28	0		12.0	0.26		
		Ba				
CHR14	2.5	3	6.0	0.5		
CHR5	5.0	4	...	0.47		
CHR15	5.0	5	6.7	0.55	0.55	3.9
CHR16	7.5	8	7.0	0.4		
CHR6	10.0	9	4.2	0.26		
CHR17	12.5	13	4.5	<0.1	<0.15	...
CHR7	20.0	21	11.0	<0.1		
		Ca				
CHR20	2.5		5.0	0.35		
CHR9	5.0	5	8.5	0.38		
CHR21	7.5		8.7	0.50	0.50	3.8
CHR10	10.0	8	8.5	0.42		
CHR11	20.0	15	11.0	0.38		
CHR23	30		6.7	0.55	0.55	2.15
CHR24	50		9.2	<0.2		
CHR26	100		3.7	<0.1		

Using a vibrating-coil magnetometer¹² the magnetic moment \bar{M} was measured as a function of \bar{H} . The "lower" critical field \bar{H}_{c1} was plotted against T ; extrapolation at both ends of this curve yields $\bar{H}_{c1}(0)$ and T_{cVM} (see Table I). The fact that T_{cH} and T_{cVM} agreed reasonably well when both were measured increases the reliability of the other T_{cH} values.

It is interesting to note that both the (BaSr)-titanate and the (CaSr)-titanate series show maximum transition temperatures somewhat higher than that of any (reduced) SrTiO₃. Superconductivity disappears earlier in the Ba series (12-15%) than in the Ca series (>30%). Neither (reduced) BaTiO₃ nor (reduced) CaTiO₃ is superconducting in the measured range of temperatures (at least not for carrier concentrations of 10^{20} cm^{-3} and less).

At the moment, we cannot present any correlation of the transition temperatures with other properties of the mixed compounds. However, a few remarks with respect to the parameters m^* and ϵ_0 may be useful. The change of lattice constant due to substitution of Ba or Ca for Sr is very small. Hence no drastic change in the electronic band structure or m^* is to be expected. However, it is possible that the substitution of Ba or Ca ions in the pseudocubic SrTiO₃ lattice lowers the symmetry and destroys the degeneracy of the six valleys. According to Cohen's theory,¹ this effect would decrease the transition temperature. The fact that an increase of T_c is observed in the mixed titanates argues against the change of band structure being the major cause.

We would like to draw attention to the possibility that the rise in transition temperature originates from the change in dielectric properties of the system. At low temperatures, the (unreduced) compounds under discussion exhibit very large values of ϵ_0 , usually associated with the dielectric behavior of a ferroelectric around the Curie temperature. Considering the suggestion that ferroelectricity and superconductivity are related phenomena,¹³ it should be pointed out that $(\text{Ca}_y\text{Sr}_{1-y})\text{TiO}_3$ is ferroelectric (and has a tetragonal lattice) in the concentration range $0.01 \leq y \leq 0.10$ with Curie temperatures between 10 and 30°K.⁴ It is possible that a similar situation exists for small Ba concentrations in $(\text{Ba}_x\text{Sr}_{1-x})$ titanate.¹⁴ Dielectric measurements on these compounds are in progress.

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CYCLOTRON RESONANCE LINEWIDTHS AND ELECTRON RELAXATION TIMES IN GALLIUM

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Chambers¹ has recently shown that if relatively few electrons participate in the resonance and $\omega_c\tau \geq 50$, then Azbel'-Kaner cyclotron resonance line shapes are independent of relaxation time while the fractional linewidth $\delta H/H \propto 1/\omega\tau$. The precise line shape and the value of the proportionality constant depend on the nature of the effective-mass extremal. It is the purpose of this note to demonstrate that Chambers's theory and the prerequisite conditions are well satisfied in gallium, and that the relaxation time of the resonating electrons can thus be measured for the first time in absolute time units. It is also shown that the temperature dependence of the relaxation time conforms to a simple model of temperature-independent impurity and crystalline imperfection scattering, plus electron-phonon small-angle scattering proportional to T^3 . While of restricted applicability, this is the only experimental method presently available for measuring transport relaxation times in metals, as opposed to mean free paths which can be determined from a variety of size effects.

The physical origin of Azbel'-Kaner line shapes may be understood from the following crude arguments. In most (relatively simple) metals in which a significant number of electrons participate in the resonance, the conductivity increases as resonance is approached,

the skin depth decreases, and fewer electrons are exposed to the rf fields resulting in an anomalously broadened line whose width bears no simple relationship to the relaxation time. In the Chambers case, however, in a complicated metal where there are relatively few electrons in a given orbit, the total conductivity does not change appreciably at resonance, the skin depth does not vary, and the line is broadened only by lifetime effects.

Gallium specimens were grown on optically flat Lucite plates which were then dissolved away; no further surface preparation was used. The sample was mounted on a choke joint to form one end wall of a TE₁₁₁ cylindrical cavity. The line examined in this note is the third harmonic of a mass series ($m^*/m_0 \sim 0.9$) observed with the external field (~ 3720 G) along the a axis in a b plane. An 8-mm spectrometer using balanced bolometer bridge detection and low audio-frequency lock-in techniques was used; the data were processed and digitally recorded with a Nuclear Data Inc. ND-181 1024-channel analyzer operated in the signal-averaging mode and further filtered, normalized, and scaled by computer.

The cyclotron resonance line calculated by Chambers for the case where the effective mass does not vary appreciably with k_H , the electron wave-vector component in the applied-