

## The Electrical Resistivity of Indium-Thallium Solid Solutions

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Electrical resistivity measurements on indium-thallium solid solutions in the composition range from indium to 50 atom percent thallium and from the boiling point of helium to room temperature are described. An anomalous behavior of the resistivity of a specimen containing 30 atom percent thallium indicates that it probably undergoes a transformation from face-centered cubic to tetragonal in the temperature interval 45–60°K.

IN connection with experiments on the superconducting properties of indium-thallium solid solutions,<sup>1</sup> we have made some measurements of the electrical resistance of these alloys at higher temperatures which will be briefly presented here. The samples used and the method of measurement are the same as previously described.<sup>1</sup> The single crystal specimens covered the composition range from indium to 20 percent thallium and the polycrystal specimens ranged from 15 to 50

percent thallium. The specific resistances at the ice point were calculated from the dimensions and observed resistances of the samples. The accuracy of specific resistances is estimated as 1 to 2 percent except in the case of the 10 percent single crystal specimen where the error is greater because the specimen was diverted to another use before accurate dimensional measurements were made. The specific resistance data at the ice-point are given in Table I. They are in fairly good agreement with the data of Meissner, Franz, and Westerhoff.<sup>2</sup>

On the single crystal specimens measurements of resistance were taken at the boiling points of helium

TABLE I. Specific resistance of In–Tl solid solutions at  $T = 273.16^\circ\text{K}$ .

Single crystals			Polycrystals		
Composition, atom percent thallium		$\rho \times 10^6$ ohm cm	Composition, atom percent thallium		$\rho \times 10^6$ ohm cm
Nominal	Actual		Nominal	Actual	
0	0	7.9	15	15.07	11.8
5	5.05	9.5	20	19.96	13.0
10	10.07	10.5*	30	30.07	15.1
15	15.09	12.0	38	37.94	16.3
20	19.89	13.1	50	49.68	17.6

\* Low accuracy, see text.

TABLE II. Resistance ratios,  $R/R_{273.16}$ , for single crystal specimens.

$T, ^\circ\text{K}$	Nominal composition, atom percent thallium				
	0	5	10	15	20
77.6	0.223	0.306	0.368	0.409	0.452
4.2	0.0080	0.106	0.179	0.240	0.287

TABLE III. Resistance ratios,  $R/R_{273.16}$  for polycrystal specimens.

$T, ^\circ\text{K}$	Nominal composition, atom percent thallium				
	15	20	30	38	50
4.20	0.2347	0.2811	0.3617	0.3855	0.3950
10.15	0.2384	0.2844	0.3650	0.3884	0.3973
13.98	0.2433	0.2899	0.3700	0.3930	0.4020
16.26	0.2471	0.2930	0.3736	0.3965	0.4051
18.17	0.2510	0.2962	0.3769	0.3993	0.4079
20.34	0.2556	0.3012	0.3808	0.4028	0.4120
46.81	0.3234	0.3622	0.4346	0.4590	0.4672
55.14	0.3452	0.3835	0.4576	0.4768	0.4849
63.26	0.3670	0.4042	0.4810	0.4950	0.5018
70.14	0.3853	0.4214	0.4965	0.5098	0.5163
77.41	0.4053	0.4391	0.5135	0.5257	0.5308
297.0	1.088	1.083	1.073	1.072	1.072

<sup>1</sup> J. W. Stout and L. Guttman, Phys. Rev. 88, 703 (1952).

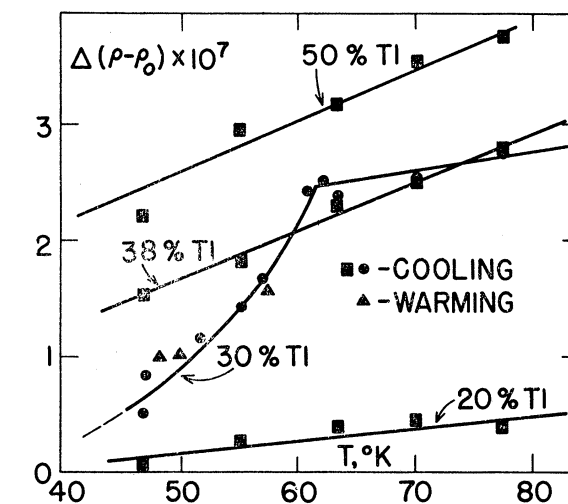


FIG. 1. Temperature variation of relative resistivity of indium-thallium solid solutions.

and nitrogen. The temperature at the nitrogen boiling point was obtained from the resistance of a copper coil calibrated against vapor pressures of oxygen. The data are shown in Table II. The ratio of the resistance at each temperature to that of the same sample at 273.16°K is given. The residual resistance of the indium specimen corresponds to an impurity content equivalent to 0.3 atom percent thallium. A spectrographic analysis of the material used showed the following impurities in weight percent: Mg, 0.01; Ca, 0.003; Cu, 0.002; Sn, 0.01; Pb, 0.001; Sb, 0.01; Si, 0.01; Fe, 0.002, Al, trace.

<sup>2</sup> Meissner, Franz, and Westerhoff, Ann. Physik [5] 13, 505 (1932).

These add up to about 0.13 *atom* percent of total detected impurity.

A more extensive series of measurements was made on the polycrystal specimens. Hydrogen or nitrogen was condensed in the inner Dewar which was ordinarily used for helium. This Dewar was surrounded by a bath of nitrogen so that heat leak into the inner dewar was very small and the temperature stability was excellent. The temperatures of the samples were calculated from the observed vapor pressure of nitrogen or hydrogen. At room temperature and the ice point the temperature was measured with a copper-constantan thermocouple. The ratio of the resistance at various temperatures to that at the ice point is given in Table III. The precision of the resistance measurements was about 0.1 percent.

An anomalous behavior of the resistivity of the 30 percent thallium specimen was observed in the nitrogen range. This is shown in Fig. 1. The ordinate is the

thermal part of the specific resistance,  $\rho(T) - \rho(0^\circ\text{K})$ , for the 20, 30, 38, and 50 percent samples, less the corresponding quantity for the 15 percent sample, which was arbitrarily taken as a standard for comparison. Although because of possible errors in the dimensional measurements the specific resistance is known only to 1 or 2 percent, for a given sample its fractional variation with temperature is known much more accurately. The anomaly in the temperature variation of the 30 percent specimen occurring over the range 45–60°K is very likely an indication that in this temperature interval the specimen is changing from a high temperature face-centered cubic form to a low temperature face-centered tetragonal one. Such an assumption fits well an extrapolation of the composition-temperature curve for the cubic-tetragonal transformation found by Guttman.<sup>3</sup>

<sup>3</sup> L. Guttman, J. Metals (Trans. Am. Inst. Mining Met. Engrs. **188**, 1472 (1950)).

## Paramagnetic Resonance in Phosphors\*

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Paramagnetic studies at 9375 Mc have been made on 32 inorganic phosphors containing paramagnetic activators. The sample is contained in a transmission cavity and the spectrum is obtained by a sweeping technique that yields the derivative of the absorption curve. Less than  $10^{-11}$  mole of  $\text{Mn}^{++}$  may be detected in cubic host crystals. The specimen in the cavity may be illuminated by ultraviolet light for observations on changes in its spectrum under these conditions, but, when illuminated, the changes observed may be attributed largely to photoconduction. The phosphors containing  $\text{Mn}^{++}$  as an activator under no illumination yield a variety of spectra. Seven of these phosphors display a single absorption line 750 to 1000 gauss wide, while four phosphors with different host crystals but all having cubic symmetry display line spectra consisting of six lines seven gauss wide but with spacings between members of from 68 to 88 gauss depending on the host crystal. Finally, two phosphors display 30-line spectra which arise because the crystal field and the applied field together serve to remove both the *I* and *S* degeneracy, whereas for cubic crystals only the *I* degeneracy is removed.

### INTRODUCTION

**E**XPERIMENTAL methods for observing paramagnetic resonance<sup>1</sup> at microwave frequencies provide means for obtaining precise and detailed information on the energy levels occupied by electrons in solids. In general, depending on the experimental technique employed, line spectra will be observed only when an adequate number of electrons with unpaired spins occur in a material and when the various factors which determine line width are favorable, such as, for example, the lifetime of the state under study or the magnitude and character of the interactions between ions and the crystal field. Such spectra should be par-

ticularly instructive when found in phosphors and other semiconductors. For example, in phosphors, the set of transitions involved in the processes of fluorescence and phosphorescence are at present imperfectly understood in any quantitative sense. Experiments on photoinduced changes in paramagnetism have been reported both for organic<sup>2</sup> and inorganic<sup>3</sup> phosphors, but these experiments make use of bulk ponderomotive effects. In the present study, the paramagnetic spectra of a number of inorganic phosphors were taken at 9375 Mc requiring magnetic fields in the 3000–3500 gauss range. The emphasis has been placed on phosphors in which small proportions of doubly ionized manganese ( $\text{Mn}^{++}$ ) are used as activators in a variety of host crystals.  $\text{Mn}^{++}$  is

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<sup>1</sup> E. Zavoisky, J. Phys. (U.S.S.R.) **9**, 211, 245, 447 (1945); **10**, 170, 197 (1946); R. L. Cummerow and D. Halliday, Phys. Rev. **70**, 443 (1946); D. M. S. Bagguley and J. H. E. Griffiths, Nature **160**, 532 (1947).

<sup>2</sup> G. N. Lewis and M. Calvin, J. Am. Chem. Soc. **67**, 1232 (1945).

<sup>3</sup> P. D. Johnson and F. E. Williams, J. Chem. Phys. **17**, 435 (1949).