Evidence for superconductive microsegregations in tin-doped bismuth

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Results on the resistivity drop around 3.7 K, observed in pulled tin-doped (0.004- to 0.3-at.% Sn) bismuth single crystals, are reported. The drop is ascribed to the superconductive transition of segregated metallic tin in the *p*-type bismuth matrix. This is confirmed by the behavior observed in a magnetic field. It is suggested that these segregations, which could not be detected by classical methods of analysis, should be taken into account in interpreting the electronic properties and the scattering mechanisms in tin-doped bismuth.

I. INTRODUCTION

Pure bismuth is a group-V semimetal with a slight band overlap, which accomodates a tiny number of electrons and holes at all temperatures. It was early realized[1,2] that the addition of very small amounts of tin, which acts as an acceptor, alters drastically the electrical resistivity of this semimetal, particularly at low temperatures. The effect of doping on the electronic structure has also been thoroughly investigated. For a review of the situation the Introduction of Noothoven van Goor's dissertation[3] may be consulted. However, in order that the results of experiments be correctly interpreted, one should know the exact amount of active acceptor sites in the samples investigated. This has been, in the past, a bone of contention and, as it will be seen hereafter, is still a matter of conjecture.

It has been reported that, when tin-doped bismuth single crystals are grown by the Czochralski method, inhomogeneity in the tin distribution is observed. This is to be associated with a very large segregation coefficient of tin in bismuth. As a consequence, an important difference which in some cases may reach an order of magnitude in the tin concentration of the pulled crystal and that of the melt, and a nonuniform tin distribution along the grown sample were evidenced.[3,4] We shall discuss here a third type of sequel of the limited solubility of tin in bismuth.

While measuring the thermal conductivity and the thermopower of tin-doped crystals, we observed a small but detectable anomaly around 3.7 K.[5] Uher and Opsal[6] independently found a small drop in the electrical resistivity of a zone-refined single crystal, and of polycrystalline Bi samples doped with Sn around the same temperature. They associated this drop with a superconducting transition of a small quantity of metallic tin segregated from the solid solution. This prompted us to extensively study the electrical resistivity of our single-crystal samples at liquid-helium temperatures.

In the present work, results on the resistivity drop observed in tin-doped bismuth single crystals grown by the pulling technique with an excess carrier concentration of $10^{18}-10^{20}$ cm^{-3} holes, are reported. The effect of an external magnetic field on the electrical resistivity in the vicinity of the superconducting transition temperature of Sn, is also investigated and reveals some interesting features.

II. EXPERIMENTAL

The tin-doped bismuth single crystals used in the present work were grown at the Philips Research Laboratories (Eindhoven) by Noothoven van Goor.[3] The excess hole density was determined by him, through measurements of the saturation of the Hall effect versus magnetic field at 4.2 K. Since, by means of radioactive tracer experiments, he established that each tin atom donates one hole to the Fermi sea, the density of tin atoms was, in principle, readily evaluated. However, as it will be shown further, this approach is not valid for concentrations higher than 10^{19} holes cm^{-3}. For this reason we shall characterize the samples hereafter by their excess hole density, as determined by Noothoven van Goor.[3]

The samples were typically rods of ellipsoidal cross section of 15 mm^2. Their axes were in the bisectrix direction. In some cases, as an homogeneity test, several portions of the sample along its length were investigated. The main characteristics of the samples

measured are shown in Table I. In only one case a significant difference was found in the residual resistance ratio (RRR), and hence in the tin contents of the different portions of the same sample. For one of the samples (Bi J 1000), in order to test whether the effect observed is due to surface or not, the crystal was etched after it was first measured. Since after etching its diameter was reduced to half its original value, this enabled us to also check radial homogeneity. Measurements performed after this etching showed that surface effects and radial inhomogeneities were both negligible.[7]

To detect the effect with sufficient accuracy, it was found necessary to measure resistances with at least 10^{-4} resolution. For this purpose a four probe dc method was used. The voltages along the different portions of the sample were measured by means of a Keithley K 174 $4\frac{3}{4}$-digit voltmeter with a 10^{-7}-volt sensitivity. The thin voltage probes consisted of either 0.1-mm-diameter sparkwelded gold or copper wires of the same diameter soldered to the sample by means of Wood's alloy. The currents, typically 0.2 to 0.6 A, generated by a source of stability of $\sim$0.005%, were measured by means of a $4\frac{1}{2}$-digit Keithley K 177 ammeter. It was checked that the sample resistance was independent of the sense and intensity of the current in the range investigated.

The sample and its holder were directly immersed in the liquid-helium bath contained in a Select-a-Stat Sulfrian magnet Dewar. Its temperature was determined from the measurement of the liquid-helium vapor pressure by means of a Wallace and Tiernan-type FA 129 manometer. The bath was stabilized with a Walker manostat to better than 10^{-3} K.

A rotating horizontal magnetic field could be applied perpendicular to the vertical sample axis by means of a conventional electromagnet. For longitudinal measurements, a vertical field was applied by means of a coil. The magnetic field was measured with a Hall effect probe to a 1% accuracy.

III. RESULTS

The results of measurements of the temperature dependence of the electrical resistivity at zero magnetic field are reported in Fig. 1. The resistivities of the samples are normalized to their value at 4.21 K. It may be seen that, for the samples of excess hole density less than 8×10^{18} cm^{-3}, no sharp drop is detected around 3.7 K within the limits of experimental error. This drop is detectable for higher excess hole densities, except for the sample with 1.22×10^{19} cm^{-3}.

In the presence of a magnetic field doped bismuth has, like the intrinsic material but to a lesser extent, a high magnetoresistance. Figure 2 represents for two samples at different temperatures the resistance, normalized to its zero-field value at 4.21 K, versus a magnetic field applied perpendicularly to the rod axes (transverse). It may be seen that, for temperatures below 3.7 K the zero-field resistivity is lower than that at 4.21 K, as expected (see Fig. 1). However, as the magnetic field is increased, the magnetoresistance curve gets closer to, then almost coincides with the curve measured above 4.21 K. It should be noted here that the magnetoresistance of the doped bismuth—if we except the observed singularity, i.e., the drop below 3.7 K and critical fields—is expected to be almost temperature independent, as it is the case for the zero-field resistivity. This is due to the fact that the residual resistivity is much higher than the ideal one below 4.21 K. For the sample exhibiting the largest zero-field resistivity drop at 3.7 K, the most accurate measurements were obtained, and we have thus been able to represent them in a more convenient way in Fig. 3. Figure 3 represents, for

TABLE I. Sample characteristics.

Sample number[a]	45			52		60		54	J 728	J 1000[b]
Sample part	*a*	*b*	*c*	*a*	*b*	*a*	*b*	*a*	*a*	*a*
RRR	1.95	2.44	3.36	4.53	4.43	6.42	6.60	6.55	10.1	11.4
Δ (10^{17} cm^{-3})	15.5[c]	12[c]	9.1[c]	80[d]	80[d]	114[d]	114[d]	122[d]	260[c]	500[c]
Resistivity at 4.21 K (10^{-6} Ω cm)	62	43	32	38	38	29	29	28	23	23
% resistance drop	...	...	...	...	...	0.85	1.4	...	0.55	0.23

[a]Except for the two last samples (J 728 and J 1000), the sample nomenclature is the same as that of Noothoven van Goor (Ref. 3).

[b]Before and after etching.

[c]Δ is determined by interpolating the RRR in the RRR vs Δ curve obtained from Noothoven van Goor's data (Ref. 3).

[d]Δ was determined by Noothoven van Goor (Ref. 3) by means of the saturation of the Hall effect.

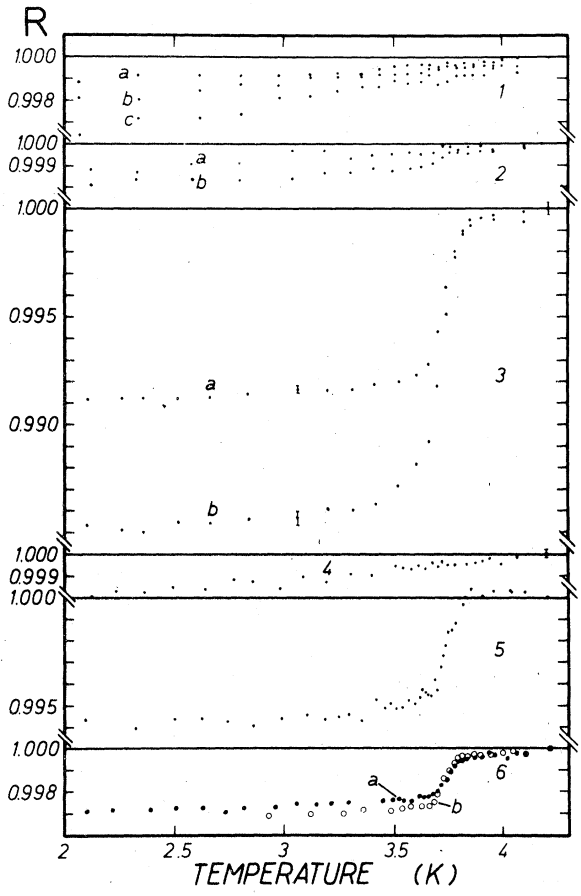

FIG. 1. Relative resistances normalized at 4.21 K vs temperature for various tin-doped samples, or sample portions, as described in Table I. The excess hole densities are, in frame 1: a = 15.5, b = 12, c = 9.1×10^{17} cm^{-3}; in frame 2: 80×10^{17} cm^{-3}; in frame 3: 114×10^{17} cm^{-3}; in frame 4: 122×10^{17} cm^{-3}; in frame 5: 260×10^{17} cm^{-3} and in frame 6: 500×10^{17} cm^{-3}. For this last case the dark circles are relative to the sample before etching and the open circles after etching.

two portions of the crystal, the ratio of the magnetoresistance at the temperature considered to that at 4.21 K at the same field versus the applied transverse magnetic field, and this for various temperatures below 3.7 K. Measurements were performed with increasing and decreasing magnetic fields and no hysteresis was detected within experimental error.

After being etched, crystal Bi J 1000 has been analyzed both in a transverse and a longitudinal magnetic field. The curves representing the restoration of "normal" resistance versus the applied field for both cases are given in Fig. 4. Note that in Figs. 3 and 4, the arrows indicate the value of the critical field for bulk tin at the temperature considered.

IV. DISCUSSION

The sharp drop in resistance observed in Fig. 1 at 3.7 K may be attributed to the superconductive transition of metallic tin regions distributed in the bismuth matrix, which short circuit it locally. The magnetoresistance curves give further evidence to this view: when the critical field for the metallic tin phase is reached, the resistance of the whole array is restored to the value it had above the critical temperature of tin, making allowance for a negligible difference due to the temperature dependence of the intrinsic resistance of bismuth in this temperautre range.

Now, it is a more delicate job to use these results in order to get precise information about the geometry and size of these tin segregations. Also, although we attribute the detected resistive drop to the metallic tin, it does not necessarily imply that the geometry of the segregated phase is the same in each sample. This is due to the fact that the segregation process depends not only on the tin contents but also on the entire thermal history of each sample, which exact details are unknown to us. We have thus

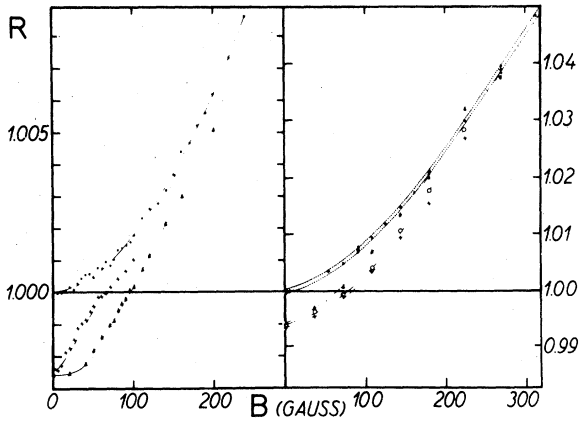

FIG. 2. Relative resistances, normalized at 4.21 K and zero magnetic field, vs magnetic induction, for two Sn-doped Bi samples at various temperatures. The left-hand side of the diagram is relative to sample J 1000 ($\Delta = 500 \times 10^{17}$ cm^{-3}): • at 4.2 K; × at 3.53 K and ▽ at 3.06 K. The right-hand side is relative to sample J 728 ($\Delta = 260 \times 10^{17}$ cm^{-3}): • at 4.20, 4.05, 4.00, 3.90, and 3.80 K; Δ at 2.97 K; ○ at 2.47 K; × at 1.89 K. For $T > 3.7$ K, the curves represent the normal magnetoresistance of the samples. For $T < 3.7$ K, at zero field, the crystals are locally short-circuited by the superconductive inclusions and normal magnetoresistance is restored when the magnetic field exceeds the critical one.

TABLE II. R and Φ values for the samples showing resistive drop.

Sample number	60		J 778	J 1000[a]
Sample part	a	b	a	a
Sample concentration 10^{17} cm^{-3} excess holes	114	114	260	500
R	0.9915	0.9860	0.9945	0.9977
Φ	2.85×10^{-3}	4.71×10^{-3}	1.84×10^{-3}	0.782×10^{-3}
Φ_Δ	0.40×10^{-3}	0.40×10^{-3}	0.92×10^{-3}	1.77×10^{-3}

[a]Before and after etching.

chosen two tentative approaches to depict two different experimental observations.

One of the easiest ways is to relate the volume density of the metallic tin phase Φ to the resistance drop. One may, for instance, imagine a situation as that discussed by Maxwell.[8] Let the dispersed phase consist of randomly-sized spheres, of infinite conductivity, randomly distributed in a medium of p-type bismuth of finite conductivity. If R is the ratio of the conductivity of the bismuth medium to the one of the array of segregated tin and bismuth, the volume density Φ of the dispersed tin phase is related to R via

$$\Phi=(1-R)/(1+2R) \quad . \tag{1}$$

Values for R, and hence for Φ, for the samples showing the resistive drop, are reported in Table II.

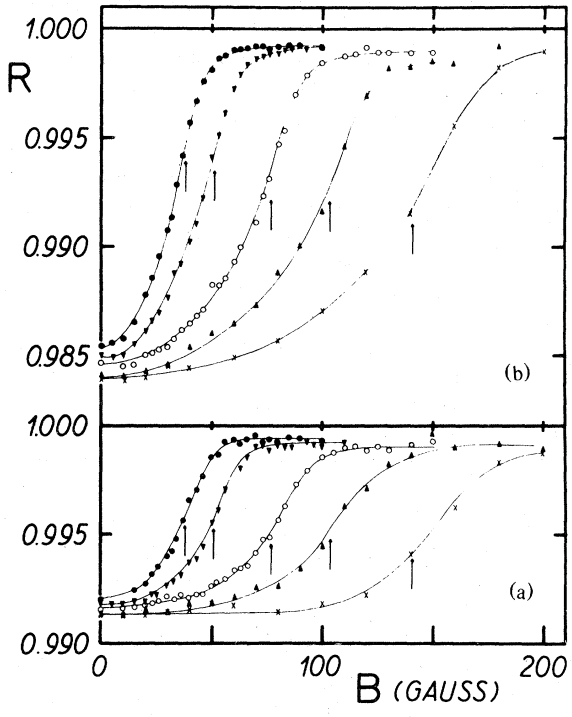

FIG. 3. Restoration of normal magnetoresistance for sample 60, ($\Delta=114\times10^{17}$ cm^{-3}); top: part b, bottom: part a. This curve represents, vs magnetic induction, the ratio of the resistance at different temperatures and fields over the resistance at the same field at 4.21 K. Temperatures: ●: 3.48 K; ▽: 3.39 K; ○: 3.22 K; Δ: 3.03 K and ×: 2.73 K. The arrows indicate the values of the critical fields of bulk tin at the corresponding temperatures.

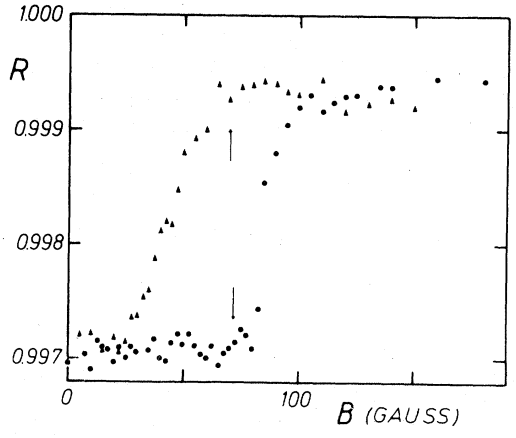

FIG. 4. Restoration of normal magnetoresistance for sample J 1000 ($\Delta=500\times10^{17}$ cm^{-3}), vs magnetic induction, for two directions of the magnetic field: Δ: field perpendicular to the sample axis (at 3.269 K); ●: field parallel to the sample axis (at 3.252 K). This illustrates the anisotropy of the inclusions. The arrows indicate the critical field of bulk tin at the corresponding temperatures. The restoration in longitudinal fields occurs at higher values than those indicated by the arrow showing the smallness (~5000 Å) of the size of the inclusions.

It is assumed that the resistance of the bismuth medium is equal to the sample resistance measured at 4.21 K. Again, here the magnitude of the effect should not be solely correlated to the dope contents, since this is not the only factor involved. In Table II, Δ is a measurement of the excess hole density, or, if we assume that tin is a monovalent acceptor, of the density of active tin-doping sites—as opposed to tin atoms in the segregated phase. From Δ, the volume density of these ionized sites Φ_Δ may be calculated and compared to the density of the tin in the segregated phase Φ (Table II). Note that this comparison has been established on the basis of spherical inclusions. If these inclusions were rods with axes parallel to the current flow, the required concentration Φ to give the same resistance drop would be smaller, and so would be the difference $\Phi - \Phi_\Delta$. Δ will thus reflect exactly the tin concentration in the crystal only when there is no metallic tin present.

From the magnetoresistance curves (Fig. 3) one may gather further information in the frame of this model. First, if the spherical model is retained, the internal field in the particles will be larger than the applied field by a demagnetization factor of $\frac{3}{2}$. In such a case, restoration of "normal" magnetoresistance would take place at higher internal fields than for bulk tin, thus indicating the smallness of the tin inclusions. Moreover, the smoothness of the transition may be due to several causes, one of them being a size distribution of the segregations. If so, with increasing field, the largest particles would turn normal first, then the smallest would turn at higher fields. The distribution of the volume density of particles of a given size a, $\phi(a) = d\Phi/da$, versus this size, could be determined from the resistance restoration pattern versus the field dR/dB_c or via Eq. (1) we have $d\Phi/dB_c$ and the critical-field dependence of the size

i.e.,

$$\phi(a) = \frac{d\Phi}{da} = \frac{d\Phi}{dB_c}\frac{dB_c}{da} \quad . \tag{2}$$

However, several other factors may influence the effect represented in Fig. 3, among which is, a pressure exerted by the bismuth matrix on the inclusions, or a small amount of bismuth contaminating the tin of the inclusions.

Another way of interpreting the results stems from the observations reported in Fig. 4. Here a strong dependence of the restoration curve on the magnetic-field direction is observed for one sample. In the longitudinal field, the transition occurs for values higher than the bulk critical field of tin at the same temperature. Again, this may eventually be attributed to the small size of the segregation. In the transverse field, normal resistivity is restored at much lower fields than it would be in bulk material; contrary to what was observed for other samples in transverse fields. As the critical field for thin films or rods is known[9] to be larger in the direction parallel to the longest dimension than in the direction perpendicular to it, this statement illustrates the possibility of an anisotropic shape of the inclusions in this sample: they may be thin rods or films parallel to the growing direction.

V. CONCLUSIONS

The experimental results reported here advocate the presence of a tin segregated phase in the bismuth matrix. Although it is established that the inclusions are of very small size, it is difficult at the present state to determine their exact shape and dimensions. It was also found unrealistic to relate in a simple way the percentage resistive drop to the dope contents. The size and geometry of the inclusions probably depend on the entire thermal history of the sample, and might be different from one sample to another. We have thus refrained from establishing a tentative general model, but instead proposed two plausible interpretations.

On the other hand, the results obtained in the present work lead to some straightforward considerations. They show that one should be very careful when dealing experimentally with tin-doped bismuth, and should be critical when surveying the related data in the literature. One obvious requirement is that, when determining the dope contents in tin-doped bismuth, one should essentially perform the analysis on the active part of the measured sample and check that the concentration is uniform all along it. It appears from the available literature that this has not always been the case. Moreover, one should not be satisfied with the obtention of a macroscopically homogeneous sample, since, as shown above, microsegregations, which do not destroy this apparent homogeneity, could be present. These microsegregations, because of their smallness and large interdistance, are not detectable by usual chemical and physical analyses. In fact, we were unable to observe them by scanning electron microscopy, and obviously the chemical analysis did not distinguish between tin in the metallic state and that acting effectively as acceptor. Also, the presence of metallic tin inclusions is not exclusively generated by the Czochralski growth process, since Uher and Opsal observed the same resistive drop with a zone-leveled single crystal.

If tin inclusions are not taken into account, at least two sources of error may sully the interpretation of

measurements on tin-doped bismuth. First, the mean concentration of tin might be quite different from that of the active acceptor sites. Second, and this might be of paramount importance when interpreting low-temperature transport measurements, segregated tin might act as relatively large scattering centers, which should be taken into account.

It is suggested that the method used here could be extended to investigate the presence of a segregated phase of superconductive material in any normal matrix, when other physical and chemical analyses fail because of lack of sensitivity.

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