

# Deviations from the Matthiessen rule in the temperature range 2 to 14°K in Sn, In, Hg and Tl containing small quantities of impurities

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The relative resistivity has been measured of diluted binary solid solutions Sn + Cd, Bi, Ga, Pb; In + Bi; Hg + An, Bi and Tl with  $\delta_0$  in the range  $(0.23 - 1.34) \times 10^{-4}$ . It is demonstrated that the Matthiessen rule breaks down in the range in which the law  $\rho_T/\rho_{293} = \delta_T \sim AT^5$  holds true. This is manifest in the growth of the coefficient A with increasing amounts of impurities in the metal. It is found that the dependence of A on the impurity concentration c is nonlinear. In Sn- and Hg-based alloys, the type of impurity has been found to affect the coefficient A, and the influence is greater the larger  $\delta_0/c$ . It is also shown that the maximum temperature up to which Bloch's law holds true diminishes with increasing impurity content.

It is known that the electric resistivity of a metal satisfies in first-order approximation the Matthiessen rule, according to which  $\rho_T = \rho_0 + \rho(T)$ , where  $\rho(T)$  is the resistivity of a metal with an ideal crystal lattice and depends on the temperature, while  $\rho_0$  is the residual resistivity and depends only on the concentration of the impurities and other lattice defects. The Matthiessen rule would obviously be always valid if the impurity atoms were to behave in the metal lattice like static defects. Actually, however, the impurity atoms vibrate, and the character of their vibrations can differ significantly from those of the host-lattice atoms. As a result, that part of the resistivity which depends on the impurity concentration will also depend on the temperature, and this means violation of the Matthiessen rule. For strongly dilute alloys one can assume, however, that the influence of the impurity atoms on the scattering of the electrons by the phonons in the metal is very small, meaning that the Matthiessen rule should hold. However, experiments performed on alloys based on Sn, Cd, In, and Al<sup>[1-4]</sup> have shown that even at low concentrations the deviations from the Matthiessen rule are quite large. It is therefore of interest to investigate this problem experimentally in greater detail, all the more since the observed deviations have not found as yet an unambiguous theoretical explanation (see, e.g.,<sup>[5-7]</sup>). The purpose of the present paper is to investigate the influence of certain concrete impurities at low concentrations on the temperature dependence of the resistance of solid solutions of Sn, In, and Hg, and also to investigate several samples of Tl of different overall purity. A characteristic of all these metals is that at a temperature  $T \leq 0.1\Theta$  ( $\Theta$  is the Debye temperature) their electric resistivity is proportional to  $T^5$ , and this agrees well with the conclusions of Kagan and Flerov<sup>[8]</sup>.

## EXPERIMENTAL TECHNIQUE

The investigations were performed on polycrystalline cylindrical samples of 1.5 - 2.5 mm diameter and ~ 80 mm length. The samples of the alloys based on Sn and In were prepared by the procedure described in<sup>[9]</sup>, and those based on Tl were prepared as in<sup>[10]</sup>. The results for the alloys based on Hg were obtained with the same samples that were investigated in<sup>[11]</sup>. To homogenize the solid solutions and to relieve the various stresses, the Sn- and In-based alloys were annealed in air for 12 days, and those based on Tl were

annealed in a helium atmosphere for two days. The annealing temperatures were  $175 \pm 5^\circ\text{C}$  for the Sn- and Tl-based alloys and  $120 \pm 5^\circ\text{C}$  for the In-based alloy. The samples were made from metals of high purity: Sn, In ~ 99.9995%, Bi, Ga, Tl ~ 99.999%, Hg  $\geq 99.9999\%$ . The impurity concentrations in the samples were determined from the ratios of the initial masses of the impurities and of the main metals. Our alloys were in the solid-solution region, as evidenced by the relative residual resistance  $\delta_0 = R_0/R_{293}$  ( $R_0$  and  $R_{293}$  are the resistances at 0 and 293°K), which was always proportional to the impurity concentration. It was also found that  $\delta_0/c$  (at.%) = 0.126, 0.072, 0.049, 0.025, and 0.20 respectively for the samples Sn - Cd, Sn - Bi, Sn - Pb, Sn - Ga, In - Bi, this being in good agreement with the data of<sup>[12,13]</sup>. Measurements of the electric resistivity were made by a potentiometer method in the temperature interval 4.2 - 14°K for alloys based in Sn and In, just as in<sup>[14]</sup>, and those for Tl and Hg were made at 1.6 - 5.1°K, as described earlier<sup>[9,11]</sup>. The temperature was determined by measuring the saturated He vapor pressure in the range 1.6 - 5.1°K, and with a germanium resistance thermometer of the TSG-2 type, calibrated at the All-Union Research Institute for Physicotechnical and Radio Measurements (VNIIFTRI) in the 4.2 - 14°K interval. The errors in the measurement of the relative resistances of the different samples, in per cent, are given in Table I.

## RESULTS AND DISCUSSION

The results of the investigations are shown in Figs. 1-3 and in Table II, from which it is seen that the relative resistance of the samples satisfies the relation

$$\delta(T) = \delta_T - \delta_0 = AT^5, \quad \delta_T = R_T/R_{293},$$

where  $R_T$  is the resistance at T°K. The decrease in the

TABLE I. Error in the measurement of the relative resistance of various samples (in %)

Sample	at 4.2°K	at 8°K	Sample	at 4.2°K	at 8°K
Sn pure	2	0.2	Sn + 0.17 at. % Ga	0.3	0.15
Sn + 0.00106 at. % Cd	1.5	0.7	Sn + 0.35 at. % Ga	0.3	0.15
Sn + 0.053 at. % Cd	0.2	0.2	Sn + 0.0115 at. % Pb	3	2
Sn + 0.0028 at. % Bi	2.5	1.0	Sn + 0.115 at. % Pb	0.7	0.6
Sn + 0.0284 at. % Bi	0.8	0.3	In pure	2.5	0.7 *
			In + 0.0044 at. % Bi	1	0.6 *

\*Error at 6°K.

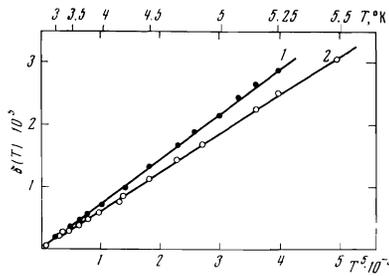


FIG. 1. Dependence of the relative resistance  $\delta(T)$  on  $T^5$  (the temperature in the lower scale is in  $^{\circ}\text{K}$ ) for two samples of thallium: 1— $\delta_0 = 3.59 \times 10^{-5}$ , 2— $\delta_0 = 2.34 \times 10^{-5}$ .

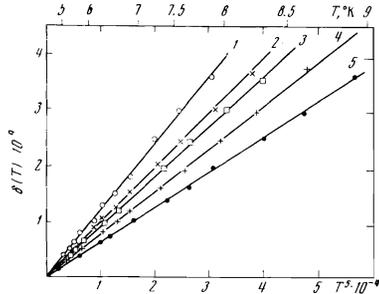


FIG. 2. Dependence of the relative resistance  $\delta(T)$  on  $T^5$  for samples of pure tin with Cd impurity (in at. %): 1—0.0528, 2—0.01056, 3—0.00528, 4—0.00105, 5—pure Sn (the solvent metal is of grade Sn-000).

slopes of the lines with increasing purity of the sample, i.e., the decrease of the constant  $A$ , is evidence that the Matthiessen rule is not satisfied.

Table II lists the values of  $\delta_0$ ,  $A$ , and of the temperature  $T_{\text{max}}$  up to which the rule  $\delta_T \sim T^5$  is valid, as well as the temperature  $T_{\text{res}}$  at which  $\delta_T$  exceeds  $\delta_0$  by 0.25%. For pure tin and for tin alloys containing less than 0.106 at. % Cd, 0.057 at. % Bi, and 0.51 at. % Ga, for pure indium, for indium alloys containing less than 0.027 at. % Bi, and for the two purest Tl samples, the values of  $\delta_0$  and  $A$  were obtained by reducing the experimental data by least squares. The deviations of the experimental values of the resistances from those calculated by the formula  $\delta_T = \delta_0 + AT^5$  lie within the limits of the errors of  $\delta_T$ . For mercury-based alloys, the coefficient  $A$  was estimated only from plots of  $\delta_T$  against  $T$ , since the temperature interval was narrow ( $\sim 1^{\circ}$ ) and there were only a few experimental points. For the remaining tin alloys, the equality  $\delta_0 = \delta_{4.2}$  is satisfied with sufficient accuracy, and for the two dirtiest In and Tl samples we have  $\delta_0 = \delta_2$  (see Table II) and there is no need to determine  $\delta_0$  by least squares. The coefficient  $A$  for these 13 alloys is obtained from the slope of the line drawn from the origin to the start of the horizontal section on the plot of  $\delta(T)/T^4$  against  $T$  (the plots were drawn up to values of  $T$  much larger than  $T_{\text{max}}$ ). In these cases it was more difficult to determine  $A$  more accurately from plots of  $\delta_T$  against  $T$  or of  $\delta(T)/T^5$  against  $T$ , owing to the large error in the determination of  $\delta(T)$  in the residual-resistance region, reached at appreciably larger values of  $T_{\text{res}}$  (see Table II) than with pure samples. The temperature interval suitable for the investigation was therefore much narrower. For the reasons indicated above, the coefficient  $A$  for the three dirtiest Sn + Cd alloys could be estimated at only 11.7–12.0.

In Table III are gathered information on the coef-

TABLE II

Metal + impurity	Impurity concentration, at. %	$\delta_0 \cdot 10^4$	$A \cdot 10^9 \text{ deg}^{-5}$	$A' \cdot 10^9, \text{ deg}^{-5}$	$T_{\text{max}}, ^{\circ}\text{K}$	$T_{\text{res}}, ^{\circ}\text{K}$
Sn-000		0.044 [2]	4.4		11.5	<3.75
		0.077 [1]	5±6			
		0.232 [2]	6.4			
		0.52 [2]	8.2			
		0.214	6.3	0		
Sn + Cd	(Sn-000)					
	0.001056	1.597	7.7	1.30	9.0	3.75
	0.00528	6.851	9.1	2.8	8.5	
	0.01056	12.92	9.9	3.60	8.4	4.0 6.0 6.5 7.3
	0.0528	68.77	12.0	5.70	8.1	
	0.1056	141.0	11.7–12	—	8.0	
0.211	297.0					
0.422	519.0					
Sn + Bi	0.00284	2.26	7.2	0.89	9.8	3.75
	0.00568	4.124	8.2	1.89	9.0	
	0.0284	19.53	9.8	3.49	8.7	~4.0 5.0 5.3 5.5
	0.0568	39.6	9.9	3.59	~9.0	
	0.1136	88.0	10.6	4.3		
0.170	124.5	11.35	5.94			
Sn + Ga	0.170	41.6	9.4	3.09	10–9.7	4.5 5.0
	0.340	84.8	10.2	3.9		
	0.5106	124	10.3	4.1	9.7	5.5
	0.851	206	—	—	9.7	6.0
Sn + Pb	1.702	402	12.3	6.0	9.5	6–7
	0.0114	5.76	7.75	1.44	<9.5	4.0 4.5
0.114	41.5	10.1	3.8			
Hg-2*		0.958	159	0	3.0	<1.5
Hg + Zn	0.00306	0.173	19.0	3.1	<2.5	0.5 1.0
	0.0306	4.15	25.0	8.9		
Hg + Bi	0.0096	2.2	2300	680	<2.5	<1.0 1.0
	0.096	19.9	2750	1160		
In-00	0.086 [3]		26.3	—	6.5	2.0
	0.33		28.3	0		
In + Bi	0.0044	9.34	36.7	8.4	6.4	<2.0
	0.0055	11.45	38.1	9.8	6.3	<2.0
	0.0275	54.8	48.2	20±2	5.5–5.8	2.5
Tl-00**		0.231	62	0	5.5	<2.0
Tl-0		0.359	71.5	9.5	5.3	1.7
Tl-00**		1.34	78	16	4.7	2.0

\*All the data for Hg-2 are given for sample No. 16, which was investigated in detail in [15]; it is assumed that  $R_{77}/R_{234} = 5.93/22.4 = 0.265$  according to Table IV of [16]. For all samples,  $\delta_0 = R_0/R_{234}$  and the constant  $A$  were determined for a resistance referred to  $R_{234}$ .

\*\*Thallium from different manufacturing batches.

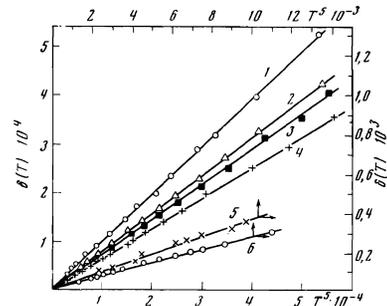


FIG. 3. Dependence of the relative resistance  $\delta(T)$  on  $T^5$  for alloys based on tin (1–4) and indium (5, 6) with Bi impurity (in at. %): 1—0.284, 2—0.0057, 3—0.0028, 4—pure Sn, 5—0.0038, 6—pure In (the solvent metal was of In-00 grade).

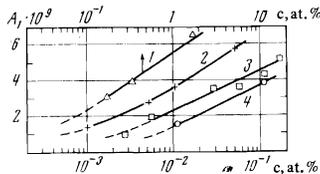
ficient  $A' = A\rho_{293}$  for different purest metals. It is seen from Table III that  $A'$  depends strongly on the type of the matrix metal, and the difference can be appreciable. The largest values are for Tl and Hg, and the smallest for Sn and Cd. This large difference between the values of  $A'$  should undoubtedly be due to singularities in the crystalline and electronic structures of the metals.

As seen from Table II, the coefficient  $A$  for a given metal increases with increasing degree of contamination with impurities (with increasing  $\delta_0$ ), as was observed earlier in the case of Sn and Cd [1] or In [3, 4]. It is also seen that with increasing  $\delta_0$  a decrease takes place in the value of  $T_{\text{max}}$ . For tin, when the impurities are introduced, this temperature drops from the maximum

TABLE III

Matrix metal	$\rho_{20}, 10^6, \Omega\text{-cm}$	$\delta_0 \cdot 10^2$	$A_1 \cdot 10^{14}, \Omega\text{-cm-deg}^{-5}$
Sn [2]	11.3	0.44	5
Cd [1]	8.45	1	6.4
In [3]	9	0.86	23.7
K [4]	6.9	27	27
Pb [1]	20.9	1.9	67
Tl	19.7	2.34	122
Hg	{ 94.2 * 22.4 * }	{ 0.138 0.58 }	3560

\*At 234°K.

FIG. 4. Dependence of the coefficient  $A_1$  on the concentration of different impurities in tin: 1—Ga, 2—Cd, 3—Bi, 4—Pb.

11.5°K for the pure metal to  $\sim 8^\circ\text{K}$ , i.e., by 3.5°K, and for indium and mercury it drops only by 0.5°K. This is apparently connected with the large difference in the Debye temperature, which equals 200, 110, 90, and 75°K for Sn, In, Tl, and Hg, respectively. For pure metals,  $T_{\text{max}}$  decreases gradually from 11.5 to 3°K on going in succession from Sn to Hg, and  $T_{\text{max}}$  decreases similarly with increasing  $\delta_0$ . On the basis of the changes of  $T_{\text{max}}$ ,  $T_{\text{res}}$ , and  $A$  given in Table II, we can conclude that the law  $\delta_T \sim T^5$  holds true in the widest range of temperatures for maximally pure metals. Then, with increasing  $\delta_0$ , the values of  $T_{\text{max}}$  and  $T_{\text{res}}$  come closer together, coinciding at a certain value of  $\delta_0$ , at which the  $\delta_T \sim T^5$  rule can no longer hold.

The violation of the Matthiessen rule is due, as indicated by Kagan and Zhernov<sup>[5]</sup>, to the "deformation" of the phonon spectrum of the solvent metal, owing to the presence of impurities. They have shown theoretically that in this case the resistance contains besides the usual term  $A_0 T^5$  an additional term  $A_1 T^5$  due to the presence of impurities, with

$$A_1 = 2A_0 c \left( \frac{m_1 - m}{m} + \frac{Z_1 - Z}{Z} \right),$$

where  $Z$  and  $m$  are the charge and mass of the host-metal ion,  $Z_1$  and  $m_1$  are the same for the impurity ion, and  $c$  is the atomic concentration of the impurity. For our alloys, which contain small amounts of Cd, Bi, and Ga impurities in tin, as indicated at the very beginning of the present section, we have  $A_1 < 1 \times 10^{-3} A_0$ , i.e., the effect is negligibly small in comparison with the observed one. It follows therefore that the cause of this increase of  $A$  is not the deformation of the phonon spectrum.

It should be noted that Masharov<sup>[6]</sup> also calculated the resistance of an alloy containing a small amount of impurities, and also obtained an additional term  $A_1 T^5$ , where  $A_1 = 2A_0 \alpha(c)$ . However, in view of the difficulty of obtaining a quantitative estimate of  $\alpha(c)$ , it was impossible to determine  $A_1$ .

The values of  $A$  for all our alloys can be represented as the sum  $A = A_0 + A_1$ , where  $A_0$  is the value of the coefficient for the solvent metal. The values of  $A_1$  are given in Table II. For the most thoroughly investigated tin-based alloys, the values of  $A_1$  are plotted in Fig. 4 as functions of the atomic concentrations of the four impurities. It follows from the last figure that  $A_1$  depends on the type of impurity and, the larger the rel-

ative residual resistance  $\delta_0/c$  per atomic per cent of the impurity, the larger the coefficient  $A_1$ . This statement, however, should be verified with a large number of impurities and with other matrix metals.

Attention is called to the fact that the dependence of  $A_1$  on  $c$  is nonlinear, viz., with increasing  $c$  the rate of increase of the coefficient  $A_1$  slows down. When  $C$  decreases without limit the value of  $A_1$  should tend to zero, and therefore all the curves should pass through the origin in the limit  $c = 0$ .

We note that the coefficient  $A$  for a given matrix metal decreases with increasing purity of the metal, mainly as a result of the decrease of the amount of dissolved impurities; unlike  $A_1$ , however, it does not tend to zero. It appears that starting with a certain sufficiently high chemical purity of the metal, the value of  $A$  will be determined by the defects of the crystal structure (the limit between the crystallites, dislocations, isotopes), as is the case for the residual electric resistivity<sup>[17]</sup>, but to a much lesser degree. One should therefore expect  $A$  to be minimal for high-purity perfect metallic single crystals.

Kagan and Zhernov<sup>[7]</sup> have recently analyzed the general character of the behavior of the resistance as a function of  $T$  and  $C$ . They took into account the fact that in an ideal metal the electron distribution function should in general contain also anisotropic terms that reflect the symmetry of the lattice. Even in the case of a spherical Fermi surface, the anisotropy of the distribution function is strongly pronounced, this being due to the anisotropy of the scattering in electron-phonon interaction, and primarily as a result of Umklapp processes. In the presence of impurities, elastic scattering by the impurities strongly suppresses the anisotropic part of the distribution function  $\varphi_{\mathbf{k}}$ . As a result, the degree of anisotropy  $\varphi_{\mathbf{k}}$  is determined by the competition between the inelastic scattering by phonons and elastic scattering by impurities. This unique "interference" between the elastic and inelastic scattering of the electrons leads to relations that are imitated by the law  $\rho \sim A(c)T^5$ , where the coefficient  $A$  depends nonlinearly on the impurity concentration, increasing with decreasing concentration<sup>1)</sup>. This agrees qualitatively with our results. A more detailed comparison of our results with the theory is impossible, because there are no final theoretical formulas suitable for the calculation of  $A$  as a function of the concentration of the dissolved impurity.

<sup>1)</sup>In Fig. 6 of [7], the places of largest and smallest impurity concentrations have been interchanged through an error.

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239