Deviations from the Matthiessen rule in the case of tin- and indium-base alloys

O. I. Lomonos, B. N. Aleksandrov, and A. P. Zhernov

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences

(Submitted March 26, 1974)
Zh. Eksp. Teor. Fiz. 67, 1114–1122 (September 1974)

The electrical resistivity of pure Sn and In, and of Sn-Cd, Sn-Bi, Sn-Ga, In-Sn, and In-Bi alloys was determined in the temperature range 4.2–55 °K. Deviations from the Matthiessen rule were determined for the investigated alloys. The deviation Δ varied nonlinearly with the concentration of the admixture c and was a nonmonotonic function of the measurement temperature T. This dependence $\Delta(T, c)$ was attributed to the isotropy of the electron distribution function which resulted from the elastic scattering by impurities. The calculations of $\Delta(T, c)$, carried out within the framework of the elastic approximation for Sn-Cd alloys, was in agreement with the experimental results.

According to the empirical Matthiesen rule, the resistivity of metals can be represented in the form

$$\rho_T=\rho_0+\rho(T), \qquad (1)$$

where ρ_0 is the residual temperature-independent resistivity due to various static lattice defects and $\rho(T)$ is the lattice resistivity of a perfectly pure ideal crystal, which depends on the measurement temperature T. Numerous experiments have shown that this rule is obeyed only in the first approximation. The observed deviations from the Matthiessen rule can be allowed for by an additional term $\Delta(T, c)$ which depends on the measurement temperature as well as on the nature and concentration of impurities (admixtures). The sign of this term can be positive or negative. Thus, in general, the resistivity of an alloy at a temperature T is

$$\rho_T=\rho_0+\rho(T)+\Delta(T, c). \qquad (2)$$

Experimental studies of the deviations from the Matthiessen rule have become possible because of the availability of sufficiently pure (99.999%) metals. A considerable number of experimental and theoretical investigations of this subject have been published and they were recently reviewed by Bass.[1] However, all the factors responsible for the appearance of the term $\Delta(T, c)$ are not yet fully understood. The available theory can describe the experimental results only qualitatively and sometimes even a qualitative description fails.

Very few studies have been made of the deviations from the Matthiessen rule exhibited by Sn alloys and the corresponding deviation in the case of In alloys has been studied only in the range < 4.5°K without considering the influence of specific impurities.[1] Thus, the first investigation of the deviation of Sn from the Matthiesen rule was carried out by Pippard,[2] who found that $\Delta(c, 273°K)/\rho_0(c) = 0.12$ for three different single crystals of Sn containing In. Later measurements were made by Alley and Serin[3] on polycrystalline samples of Sn containing one of the following three impurities: In (2.5–5.7 at.%), Sb (1.85–8.0 at.%), and Bi (0.8–10 at.%). Alley and Serin studied the deviation at 77 and 198–348°K on the basis of the relative resistivity and found that the deviation was proportional to the relative residual resistivity, independent of the nature of the impurity and of temperature (in the $T > 200°K$ range). Reich and Kinh[4] measured the resistivity of Sn single crystals of different degrees of purity (judged by the value of ρ_0) in the range 375–295°K. They found that between 3.74 and 4.22°K the resistivity obeyed the law $\rho_T = \rho_0(c) + AT^5$ and the coefficient A increased with increasing impurity concentration.

Bruckbuchler and Reynolds[5] investigated the deviation from the Matthiessen rule exhibited by Sn samples at 77 and 273°K in the presence of one of the following three impurities: In (0.1–2.5 at.%), Sb (0.05–1.8 at.%), and Zn (≤ 0.6 at.%). They also failed to detect any dependence of the deviation on the nature of the impurity and found that, at 273°K the deviation was 1.7–1.8 times greater than at 77°K. Finally, Karamargin et al.[6] investigated the deviation from the Matthiessen rule exhibited by Sn single crystals (c axis perpendicular to the measuring current), containing Cd (0.24–0.97 at.%); this study was carried out in the temperature range 4.2–80°K. They found that the deviation could be described approximately by the equation $\Delta(T, c) = 5.2 \cdot 10^{-5}\rho_0 T^2$. Since, in most cases, the deviations were investigated at fixed temperatures, which was the least interesting approach, the amount of information on tin alloys obtained in this way was not large. Therefore, our purpose was to investigate the influence of Cd, Bi, and Ga impurities on the deviation of Sn from the Matthiesen rule and the influence of Bi and Sn impurities on the corresponding deviation exhibited by In. The study was carried out in the range 4.2–55°K.

EXPERIMENTAL METHOD

Our investigation was carried out on polycrystalline cylindrical samples of 1.5 mm diameter and 70–80 mm long. All the alloys were prepared from high-purity Sn (OVCh-000 grade with a relative residual resistivity $\delta_0 = \rho_0/\rho_{290} = 2.2 \cdot 10^{-5}$) and high-purity In (In-00 grade with $\delta_0 = 3.3 \times 10^{-5}$). The method used in the preparation of the alloys was described in detail in[7]. Some of the samples used in the present study had also been investigated before.[8] The concentrations of the impurities (admixtures) in the samples were governed only by the ratio of the original masses of the impurity and solvent metal. In all cases, the value of δ_0 was a linear function of the impurity concentration c, which indicated that our alloys were solid solutions. The values of δ_0/c (at.%) obtained bv us were in good agreement with the published values.[9, 10]

The resistivity was measured in the 4.2–55°K range using a cryostat similar to that described in[11]. We studied simultaneously up to five samples which—together with resistance thermometers—were placed in recesses on a horizontal duraluminum substrate lying at the bottom of a copper block. This enabled us to assume that the temperature of each thermometer was equal to the temperature of the sample to which it was attached. Measurements on pure Sn or In were carried out using two samples in the form of wires of 1.2 mm diameter and 400 mm long. These wires were formed into helices and placed in the recesses of a massive brass substrate.

Between 4.2 and 12°K the temperature was measured with a TSG-2 germanium thermometer; between 12 and 55°K the temperature was measured with a TSPN-2A platinum resistance thermometer, calibrated at the All-Union Scientific-Research Institute for Physicotechnical and Radio Engineering Measurements. The resistances of the samples and thermometers were measured using a R-348 potentiometer and the usual potentiometric circuit. The measuring current in the samples at temperatures of 4.2-55°K was 1 A. The error in the determination of the required resistance did not exceed ± 0.1% at the lowest temperatures and ± 0.02% at higher temperatures.

The current leads were soldered to the samples and the potential leads were attached by the spot-welding method. The resistivity at 290°K was found by measuring the resistance and then determining the distance (with an IZA-2 comparator) between the potential leads to within ± 0.05 mm. The samples were then cut at the points of location of the potential leads and weighed to within ± 0.1 mg using an ADV-200 balance. The cross-sectional area of a sample was determined to within 0.2%, knowing the mass of the sample, its length and density of pure tin (7.30 g/cm^3) and indium (7.31 g/cm^3) at 20°C. We assumed that the density of the alloys was equal to the density of the pure metal matrices because the concentration of the impurities did not usually exceed 0.5 wt.%. Consequently, the error in the determination of the geometric factor was ~0.35%. No corrections were made for the change in the geometric factor due to cooling from room temperature to 55–4.2°K because such a correction was judged to be much smaller than the observed effects. Thus, the resistivity of the samples was determined with an error not exceeding ± 0.5%.

In the determination of the deviation from the Mattiessen rule, it was necessary to know the temperature-dependent resistivity of the alloy and of the pure solvent metal. Therefore, we found the relative residual resistivity δ_0 for each sample. The measurements indicated that, in all cases, with the exception of In + 0.027Bi and In + 0.19Sn, the 4.2°K resistivity was equal to the residual value, i.e., $\delta_{4.2} = \delta_0$.[8] For each alloy, we estimated the temperature T_{res} at which δ_T exceeded δ_0 by ~0.25%. In the case of pure metal solvents and two In alloys, the value of δ_0 was found from the equation $\delta_T = \delta_0 + AT^5$, which was valid in the range $T \leq 11.5$°K for Sn and $T \leq 6.5$°K for In.[8] The reliability of the results was increased by preparing two samples from pure Sn and In under the same conditions. The alloy samples were then made from this pair of samples. The measurement of δ_T for each pair revealed a good agreement in the temperature range 4.2–55°K.

RESULTS AND DISCUSSION

We determined the resistivity of pure Sn and In and of dilute alloys based on these metals. This was done in the temperature range 4.2–55°K and the measurements were repeated on each sample at least three times throughout this range. Figure 1 gives typical temperature dependences of the resistivity of pure Sn and of its alloys with different amounts of the Cd impurity. It is clear from this figure that, as the impurity concentration increases, so does the temperature T_{res} at which we can assume that $\delta_T = \delta_0$. The values of δ_0, ρ_{290}, and T_{res} are listed in Table I together with the alloy composition.

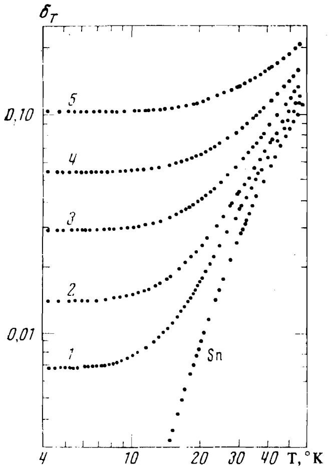

FIG. 1

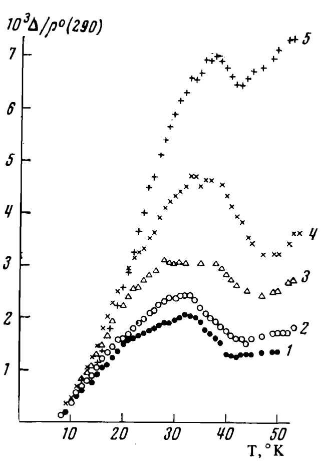

FIG. 2

FIG. 1. Temperature dependences of the relative resistivity δ_T of pure Sn and of its alloys with Cd: Sn denotes pure tin (OVCh-000 grade); 1) 0.053 at.% Cd; 2) 0.106; 3) 0.211; 4) 0.422; 5) 0.845.

FIG. 2. Temperature dependences of the deviation from the Matthiessen rule $\Delta/\rho^0(290)$ for Sn with Cd impurities. Curves 1–5 have the same meaning as in Fig. 1.

TABLE I

Alloy composition	Impurity concentration, at.%	$\delta_0 \cdot 10^2$	ρ_{290}, μΩ·cm	T_{res}, °K
Sn — Cd	0,053*	0.687	11.40	4.0
	0,106*	1.41	11.47	6.0
	0.211*	2.97	11.60	6.5
	0.422*	5.49	11.98	7.3
	0.845	10.40	12.64	8
Sn — Bi	0.057*	0.41	11.44	5.0
	0.114*	0.88	11.51	5.3
	0,170*	1.24	11.54	5.5
	0.294	2.10	11.62	5.7
Sn — Ga	0,340*	0.85	11.50	5.0
	0.851*	2.06	11.65	6.0
	1.702	4.02	11.88	6.4
In — Bi	0.027*	0.55	9.00	2.5
	0.110	2.20	9.14	4.7
	0.164	3.18	9.28	5.3
	0.275	5.270	9.53	5.5
In — Sn	0.193	0.83	9.09	<4
	0.484	2.00	9.25	5

*The same samples as in [8].

Deviations from the Matthiesen rule were calculated for each alloy as the relative change in the resistivity compared with that of a pure metal:

$$\frac{\Delta(T,c)}{\rho^0(290)} = \frac{\Delta\rho^1(T) - \Delta\rho^0(T)}{\rho^0(290)} = \frac{(\rho_T{}^1 - \rho_0{}^1) - (\rho_T{}^0 - \rho_0{}^0)}{\rho^0(290)}, \quad (3)$$

where the superscripts 1 and 0 refer to the alloy and pure metal, respectively. The value of $\Delta(T, c)$ for each alloy was found from the smoothed-out dependences of $\delta(T)$ on T for the alloy and pure metal. The values of $\rho(T)$ and ρ_0 were deduced by multiplying $\delta(T)$ and δ_0 by the resistivity $\rho(290)$ of the sample in question In the case of pure Sn, the value of $\rho(290)$ was 114. μΩ · cm, whereas, in the case of In, it was 9.0 μΩ · cm. The results obtained in this way are plotted in Figs. 2–6.

It is clear from these figures that in all cases the quantity $\Delta(T, c)/\rho$ (290) depends nonlinearly on the impurity concentration and varies monotonically with rising temperature T; for the majority of the alloys, there is a definite maximum in the 25–35°K range. This is in good agreement with the results of Reich and Kinh,[4] who investigated the deviation from the Matthiessen rule and found that $\Delta(T, c)$ reached its maximum in the region of $\sim$25°K. However, it should be pointed out that the results of Reich and Kinh were deduced from the extrapolated values of the resistivities of the alloys and pure metals because their measurements were restricted to the intervals 3.75–4.2, 13.8–20.4, and 56–90°K.

The presence of a maximum in the region of $\sim$30°K in the dependence of $\Delta/\rho^0(290)$ on T for the Sn + 0.21 at.% Cd alloy (Fig. 2) was in good agreement with a maximum of a similar curve for Sn + 0.24 at.% Cd reported by Karamargin et al.,[6] although it was surprising that they did not detect maxima for two other alloys containing 0.41 and 0.57 at.% Cd. The curve reported for Sn + 0.97 at.% Cd in[6] was a monotonic function of T; this was not surprising because our Figs. 2-4 indicated that the maximum became less pronounced with increasing impurity concentration.

It is clear from all the figures that the maximum shifted toward lower temperatures with increasing impurity concentration, in qualitative agreement with the theoretical predictions made in[12]. A quantitative comparison was difficult to make because the maxima were strongly flattened. It is also clear from the figures that in the case of all the investigated alloys, with the exception of the two samples of the Sn-Bi alloys with the lowest impurity concentrations, the derivative was $d[\Delta(T, c)/\rho^0(290)]/dT > 0$ at temperatures $T \geq 45$°K, irrespective of the sign of the difference between the valences ΔZ of the impurity and matrix, which was not in conflict with the results reported in[5] for Sn-Sb, Sn-In, and Sn-Zn alloys, although for some of these alloys measurements at $T > 50$°K would be required to increase the reliability.

According to the current theories, the deviation from the Matthiessen rule could be due to any one of the following causes: 1) a change in the energy band structure and deformation of the phonon spectrum as a result of alloying; 2) inelastic scattering of electrons by the excess potential of vibrating impurity ions (this phonon-impurity scattering is due to a periodic displacement of impurities by a lattice wave[13-16] and to the deformation of the impurity potential by stresses in the lattice[15, 17]); 3) a two-band effect[18] in which two or more groups of electrons participate in the conduction process (the relaxation times for the scattering of electrons by phonons and impurities may be different for electrons belonging to different groups); 4) the isotropy of the electron distribution function as a result of the presence of impurities (this function is anisotropic for the pure metals[12]).

In our alloys, the difference between the masses of the impurity and solvent atoms is either zero (Sn-Cd, In-Sn) or does not exceed a factor of two. Therefore, it follows from the graphs in Fig. 1 given in[16] that the deviation from the Matthiessen rule due to the deformation of the phonon spectrum as a result of the difference between the atomic masses cannot be decisive in the case of our alloys. Since the impurity concentration in most of our alloys is low (≤ 0.5 at.%), it follows that the changes in the energy band structure of the host metal can also be ignored.

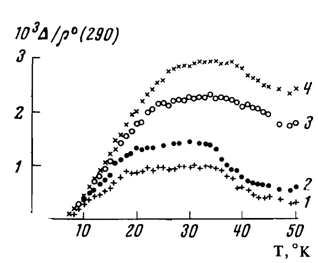

FIG. 3

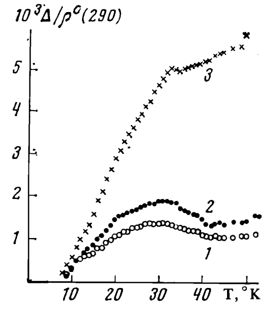

FIG. 4

FIG. 3. Temperature dependences of the deviation from the Matthiessen rule $\Delta/\rho^0(290)$ for Sn with Bi impurities: 1) 0.057 at.% Bi; 2) 0.114; 3) 0.170; 4) 0.294.

FIG. 4. Temperature dependences of the deviation from the Matthiessen rule $\Delta/\rho^0(290)$ for Sn with Ga impurities: 1) 0.340 at.% Ga; 2) 0.851; 3) 1.702.

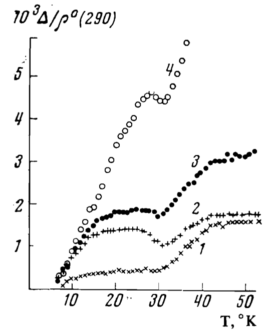

FIG. 5

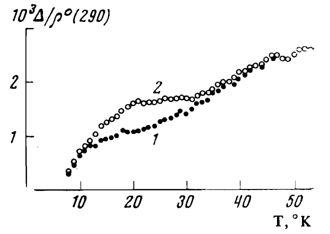

FIG. 6

FIG. 5. Temperature dependences of the deviation from the Matthiessen rule $\Delta/\rho^0(290)$ for In with Bi impurities: 1) 0.027 at.% Bi; 2) 0.110; 3) 0.164; 4) 0.275.

FIG. 6. Temperature dependences of the deviation from the Matthiessen rule $\Delta/\rho^0(290)$ for In with Sn impurities: 1) 0.193 at.% Sn; 2) 0.484.

The phonon-impurity scattering is important in the temperature range where $w\tau_i \gg 1$ (w is the thermal phonon frequency and τ_i the electron relaxation time), i.e., in practice, such scattering is important in the range where $\rho_0 \gg \rho(T)$. According to the theory,[13-17] this scattering causes a deviation from the Matthiesen rule proportional to cT^2 and cT^4 (c is the impurity concentration). In the case of our tin alloys, the inequality $\rho_0 \gg \rho(T)$ is satisfied at $T < 20$°K and the deviation in the 10–15°K range is roughly proportional to $cT^{2.8}$. Therefore, we may assume that, in this range of temperatures, the deviation is due to the phonon-impurity scattering. A more definite conclusion is not yet possible.

The presence of the maxima of the dependences $\Delta(T, c)$ obtained for tin alloys can be explained qualitatively by a two-band model because the anisotropy of the electrical and thermal conductivity of Sn suggests that there are two groups of electrons that dominate the conduction process: one is located near the tetragonal axis and the other is a series of large groups perpendicular to this axis.[19, 20] However, quantitative esti-

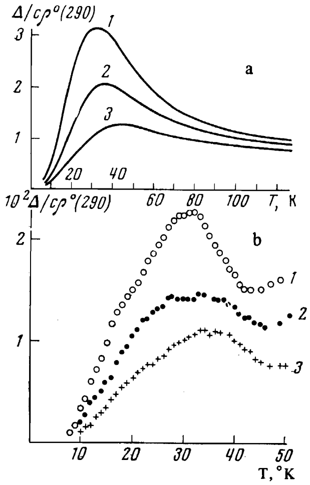

FIG. 7

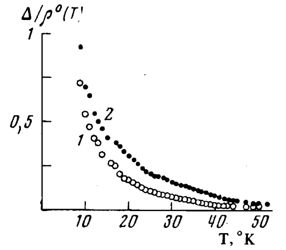

FIG. 8

FIG. 7. Calculated (a) and experimental (b) temperature dependences of the deviation from the Matthiessen rule $\Delta/c\rho^0(290)$ for Sn with Cd impurities: 1) 0.106 at.% Cd; 2) 0.211; 3) 0.422.

FIG. 8. Contribution of $\Delta(T, c)$ to the ideal resistivity of pure tin $\rho^0(T)$ at various temperatures, plotted for two alloys containing 0.053 (curve 1) and 0.42 (curve 2) at.% Cd.

mates cannot be obtained because it is difficult to determine the electron relaxation times in different scattering processes.

We shall now consider the last of the possible causes of the deviation from the Matthiessen rule. Kagan and one of the authors of the present paper[12] suggested that the distribution function of electrons in a metal should be anisotropic, mainly due to the anisotropy of the inelastic scattering in the electron-phonon interaction. They used the two-moment approximation and allowed for the anisotropy of the distribution function, which reduces considerably the resistivity of an ideal metal in a certain range of low temperatures, compared with the usual one-moment approximation. Elastic scattering by impurities should strongly reduce the anisotropic part of the distribution function. This special interference between the elastic and inelastic scattering of electrons should result in a strong nonlinear dependence of the resistivity on T and c, reported by many workers.[11, 21, 22] The analysis made by Kagan and Zhernov[12] of the expression obtained for the deviation from the Matthiessen rule indicated that at very low and high temperatures the deviation $\Delta(T, c)$ should be proportional to c. At intermediate temperatures, the deviation should have a strong maximum, whose position should not be greatly affected by the impurity concentration.

We calculated the deviation for tin alloys using the theory given in[12]. The Fermi surface was assumed to be spherical, the phonon spectrum taken to be isotropic, and the potential was taken in the screened Coulomb form. The resistivity due to the elastic scattering by impurities was assumed to be equal to the residual resistivity. Figure 7 shows the experimental (b) and calculated (a) temperature dependences of the deviation from the Matthiessen rule for three Sn-Cd alloys. The calculated values of $\Delta/c\rho^0(290)$ are given in relative units. It is clear from Fig. 7 that the experimental results could be explained qualitatively by the theory given in[12]. Judging by the dependences of Δ on T exhibited by all the investigated alloys, we could assume that the main cause of the observed nonlinear dependences was the isotropy of

TABLE II

T, °K	$\rho^0(T)\cdot10^2$, μΩ·cm	T, °K	$\rho^0(T)\cdot10^2$, μΩ·cm	T, °K	$\rho^0(T)\cdot10^2$, μΩ·cm	T, °K	$\rho^0(T)\cdot10^2$, μΩ·cm
7	0,114	19	8,64	29	28,73	41	66,01
8	0.239	20	10.10	30	31,35	42	69.54
9	0.433	21	11.74	31	33,97	43	72,96
10	0.741	22	13.45	32	36.76	44	76,61
11	1.163	23	15.39	33	39,56	45	80.26
12	1.710	24	17.38	34	42.64	47	87,89
13	2,360	25	19.44	35	45,83	49	95,53
14	3.135	26	21.66	36	49.02	50	99.41
15	4.036	27	23,83	37	52,21	52	107.1
16	4,902	28	26,22	38	55.52	53	110.8
17	6.099			39	58,93	55	118.6
18	7,296			40	62,47		

the electron distribution function resulting from the introduction of impurities.

We shall now comment briefly on the indium alloys. It is clear from Figs. 5 and 6 that the nature of the deviation from the Matthiessen rule exhibited by the In-Sn and In-Bi alloys is somewhat similar to the behavior of the tin alloys, but the maxima are less pronounced. The temperature T* at which these curves have a maximum is approximately 20-25°K, whereas in the case of the tin alloys we find that T* ~ 30 ± 5°K. Bearing in mind that the Debye temperature of In is Θ 110°K and that of tin is $\Theta \approx 200$°K, we find that $T^* \approx \Theta/5$, in agreement with the published values.[1] We may assume that the nonmonotonic dependences of Δ on T and c, observed for the tin and indium alloys, are of the same origin, but this would require a more careful study.

We shall now consider the dependences of ρ_T on T obtained for the pure metals at low temperatures. Our dependences of $\Delta/\rho^0(290)$ on T show clearly that Δ varies with the temperature and impurity concentration but it is difficult to estimate the degree of influence of Δ on the dependence $\rho^0(T) = f(T)$. Therefore, Fig. 8 gives a typical dependence of $\Delta/\rho^0(T)$ on T for two alloys containing Cd. Similar dependences can be plotted for the other alloys using the data in Figs. 2–4 and in Table II, which gives the values of $\rho^0(T) = f(T)$ for pure tin.

It is clear from Fig. 8 that the deviation from the Matthiesen rule at 50°K is only 2–4% of $\rho^0(50)$ for tin and at 20°K it is 16–30%. Consequently, the role of the contribution of Δ increases when the temperature is lowered and is greater for the less pure alloys. Hence, we can conclude from Fig. 8 that to investigate the dependences of ρ_T on T we need metals of higher purity (with lower values of ρ_0) if the investigation is to be carried out at low temperatures (below the Debye temperature). Otherwise, the deviation from the Mathiessen rule strongly distorts the real temperature dependence $\rho^0(T)$ of a pure metal at, for example, helium temperatures. This has been confirmed by many experimental investigations of metals with different values of ρ_0. On the other hand, the deviation from the Mathiessen rule is important even at room temperatures, when ρ_0 is comparable with $\rho^0(300)$ (see, for example,[22]). It is worth noting that all the nonmonotonic dependences which can be seen clearly in Fig. 2 are practically absent from Fig. 8

---

[1] J. Bass, Adv. Phys. 21, 431 (1972).
[2] A. B. Pippard, Philos. Trans. R. Soc. London A **248**, 97 (1955).
[3] P. Alley and B. Serin, Phys. Rev. **116**, 334 (1959).
[4] R. Reich and V. Q. Kinh, C. R. Acad. Sci. (Paris) **256**, 4432 (1963).
[5] F. V. Burckbuchler and C. A. Reynolds, Phys. Rev.

175, 550 (1968).
[6]M. C. Karamargin, C. A. Reynolds, F. P. Lipschultz, and P. G. Klemens, Phys. Rev. B6, 3624 (1972).
[7]B. N. Aleksandrov, V. V. Dukin, and V. V. Derevyanchenko, Fiz. Metal. Metalloved. 33, 584 (1972).
[8]O. I. Lomonos and B. N. Aleksandrov, Zh. Eksp. Teor. Fiz. 64, 2248 (1973) [Sov. Phys.-JETP 37, 1137 (1973)].
[9]B. N. Aleksandrov and V. V. Dukin, Fiz. Metal. Metalloved. 34, 739 (1972).
[10]G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. 114, 719 (1959).
[11]A. C. Rose-Innes and R.F. Broom, J. Sci. Instrum. 33, 31 (1956); G. Kh. Panova, A. P. Zhernov, and V. I. Kutaĭtsev, Zh. Eksp. Teor. Fiz. 53, 423 (1967) [Sov. Phys-JETP 26, 283 (1968)].
[12]Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. 60, 1832 (1971) [Sov. Phys.-JETP 33, 990 (1971)].
[13]S. Koshino, Prog. Theor. Phys. 24, 484, 1049 (1960).
[14]P. L. Taylor, Proc. Phys. Soc. Lond. 80, 755 (1962); Phys. Rev. 135, A1333 (1964).
[15]P. G. Klemens, J. Phys. Soc. Jap. Suppl. 18, 77 (1963).
[16]Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. 50, 1107 (1966) [Sov. Phys.-JETP 23, 737 (1966)].
[17]A. B. Bhatia and O. P. Gupta, Phys. Lett. A 29, 358 (1969).
[18]J. M. Ziman, Phys. Rev. 121, 1320 (1961).
[19]P. G. Klemens, C. Van Baarle, and F. W. Gorter, Physica (Utr.) 30, 1470 (1964).
[20]M. C. Karamargin, C. A. Reynolds, F. P. Lipschultz, and P. G. Klemens, Phys. Rev. B5, 2856 (1972).
[21]J. S. Dugdale and Z. S. Basinski, Phys. Rev. 157, 552 (1967).
[22]R. S. Seth and S. B. Woods, Phys. Rev. B2, 2961 (1970).

Translated by A. Tybulewicz
124