Magnetostriction in superconducting indium lead alloys

Magnetostriction in Superconducting Indium Lead Alloys

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Abstract. The magnetostriction and the magnetization have been measured in a series of indium alloys having a lead content ranging from 0 to 25 at.%. From the measured curves – of which some typical are presented – the critical temperature, T_c, the critical field at absolute zero, H_0, the coefficient of the electronic specific heat, γ, the Ginzburg-Landau parameter, $\varkappa$, and, in particular, their volume dependences are deduced. These parameters are related to variations in the crystal structure, the Fermi surface, and the mass enhancement constant λ.

Introduction

We measured simultaneously the magnetostriction and the magnetization of various polycristalline indium alloys ranging between 0 and 25 at. % Pb, as functions of the external field at different temperatures between 1.3 K and 4.2 K. These alloys are type-I superconductors for a lead content smaller than ~4 at.% and type-II-superconductors above 4 at.% Pb. The thermodynamics that relate the magnetostriction to the magnetization and to the stress dependences of the volume, V, the critical field H_c and the Ginzburg-Landau parameter $\varkappa$ are given in previous papers [1, 2]. This paper is concerned mainly with the further discussion of these data and their relation to crystal structure variations.

We have chosen In-Pb alloys for these investigations because of a) an existing general knowledge on this alloys system and b) strong structure variations with lead content that are expected to have an influence on the superconducting properties. These measurements of the critical temperature T_c of a series of specimens have been made by Merriam [3] and Meissner, Franz and Westerhoff [4], the magnetization curves have been studied by Gygax [5] and by Noto, Muto and Fukuroi [6]. Gygax has also measured the residual resistivity at 4 K. The structure of In-Pb alloys has been studied by Tyzack and Raynor [7], by Moore, Graham, Williamson and Raynor [8] and by Merriam [9]. They found a tetragonal crystal structure that changes lattice constant ratio, c/a, from $c/a > 1$ to $c/a < 1$ at about 13 at.% Pb. Further c/a has a maximum near 7 at.% Pb and a minimum near 20 at.% Pb.

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Apparatus and Sample Preparation

The magnetostriction was measured by a capacity method and the magnetization by a flux meter. Details of the apparatus are given elsewhere [2]. The same paper also describes the preparation and the measurement of ellipsoidal specimens 50 mm long and with axial ratio 1:8, which are made of indium with 5, 9, 15, 20 and 25 at.% lead. All the thermodynamic properties measured on these samples are presented below.

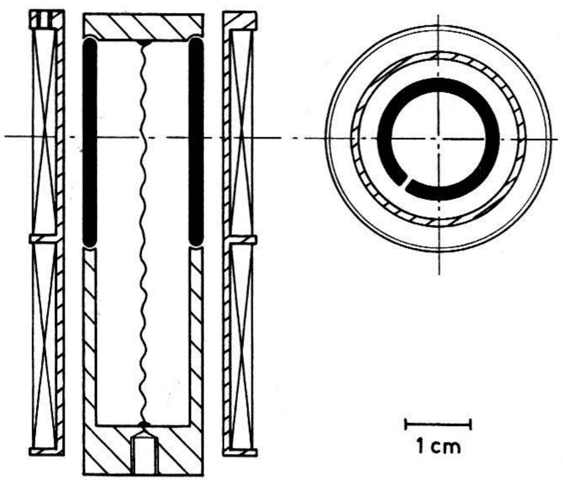

Figure 1
Cylindric sample and pick-up coils as they were put in the measuring capacitance. The actual specimen is the black hollow slit cylinder.

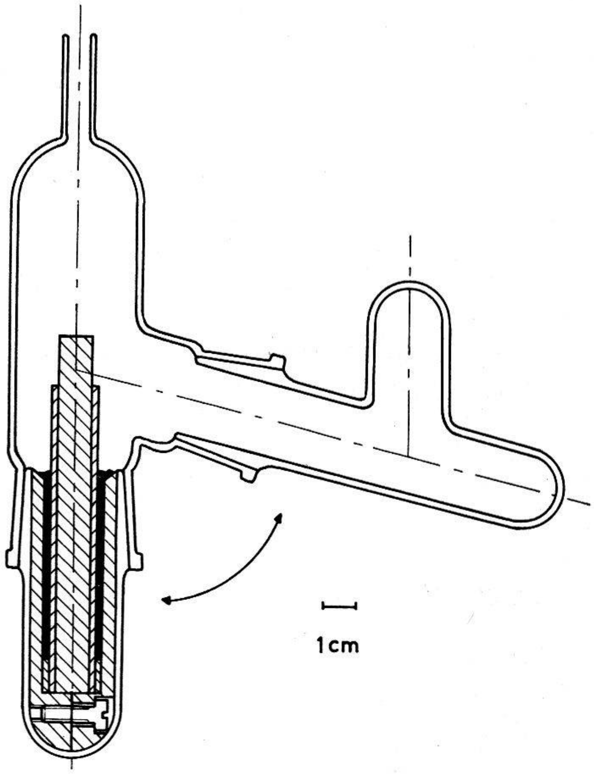

Figure 2
Evacuable vessel made from pyrex glass for melting and mixing the alloy, and casting the cylindric sample.

Specimens of indium with 0, 1, 2, 3, 4.1, 5, 6, 7, 9 and 10 at.% lead were hollow slit cylinders as shown in Figure 1. Their length was 33 mm, the outer diameter 18 mm, and the wall thickness 2 mm. These specimens were prepared by mixing the proper amounts of lead and indium in a y-shaped pyrex tube as shown in Figure 2. The two metals were melted together and poured from one part to the other about 100 times in an attempt to obtain a homogeneous mixture. Afterwards the hollow cylinder was cast in the mold shown in Figure 2. Its core consisted of a slightly conical brass cylinder surrounded by a teflon tube. The outer part of the mold was composed of two half cylinders made from brass and coated with 'dag', a suspension of graphite in alcohol, to avoid sticking of the specimen.

The specimens were then cut to the proper length and rounded at the end on the lathe. Afterwards they were slotted on one side to get a singly connected body, and cemented to the copper parts using epoxy resin. The completed samples were tempered for 1 week at 145 °C under vacuum. After tempering, the copper end plates of the samples were lapped flat and parallel. Some specimens were electropolished on the outeside in 1/3 nitric acid and 2/3 methyl alcohol solution and in two cases even electroplated with copper. This treatment had no effect on the thermodynamic parameters discussed in this paper.

During a run, the sample was located inside one of two oppositely wound pick-up coils (see Fig. 1) to measure the magnetization. The copper plate at the upper (free) end of the sample was the lower plate of a parallel plate disc capacitor (with guard ring), by which the magnetostrictive length change was detected. The sensitivity was about 0.3 Å in Δl. The magnetic field was directed parallel to the axis of the specimen and increased and decreased at constant temperature and typically within a few minutes. After each cycle the sample could be heated above the critical temperature, T_c, to expel the trapped flux.

Measurements at Constant Temperature

Figures 3 and 4 shows magnetostriction and magnetization curves at 1.3 K of some of the investigated In-alloys with 0–25 at.% Pb. For more than about 4 at.% Pb the specimens are type-II superconductors. The curves in Figure 3 are taken on specimens of the hollow slit cylinder type, whereas in Figure 4 the specimens are ellipsoids. There is no important difference between measured curves for the two

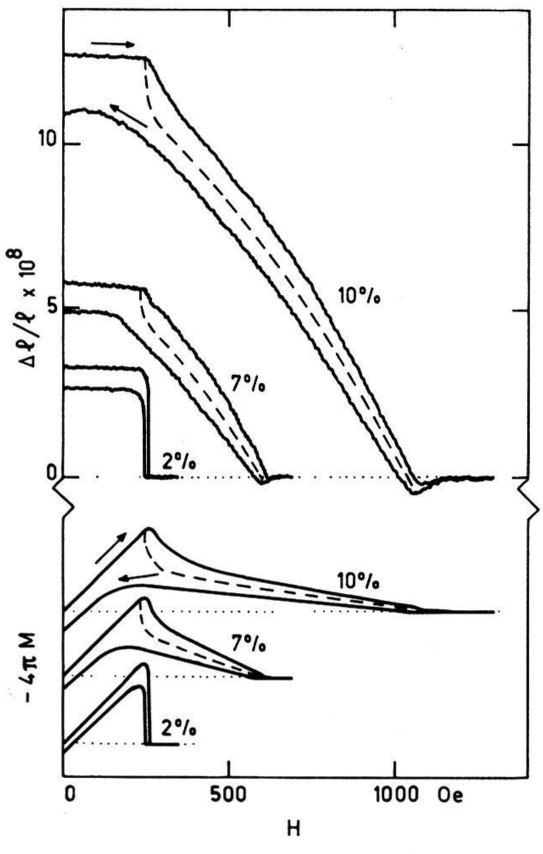

Figure 3
Magnetostriction and magnetization curves of some typical alloys measured at 1.3 K in hollow cylinders.

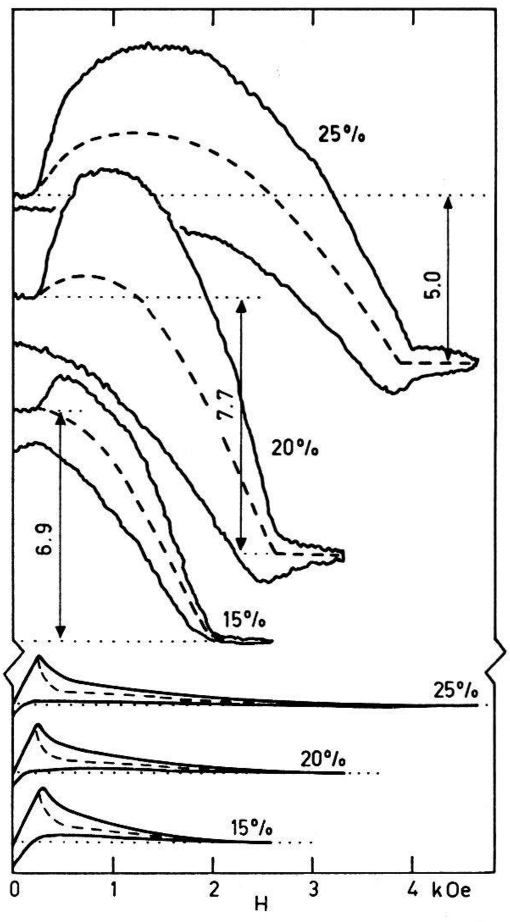

Figure 4
The same as in Figure 3 for alloys of higher lead content, measured at 1.3 K in ellipsoids of 50 mm length and 6.25 mm diameter.

types of specimens. This may be seen by comparison of the magnetostriction and magnetization curves of In-9 at.% Pb in two previous papers [1, 10].

The hysteresis of type-II superconductors in Figure 3 and 4 is mainly due to superconducting surface currents in the mixed state as has been shown elsewhere [2]. Assuming that both diamagnetic and paramagnetic surface currents have equal critical values, the dashed curves can be constructed. They are assumed to be the magnetostriction and the magnetization in the absence of surface screening currents and remaining bulk hysteresis (assumption 1). Since the magnetostriction due to surface currents is nearly proportional to the external field, the hysteresis is much larger in specimens with high upper critical fields, H_{c2}, as observed in samples with high lead content.

For the present discussion, only the dashed curves are considered. We shall now try to explain them thermodynamically.

The integration of the dashed magnetization, M, gives

$$\int_0^{H^*} V\, M(H')\, dH' = V \frac{H c^2}{8\pi} = G_n(H^*) - G_s(0)\,, \tag{1}$$

where V is the volume; H^* is the smallest field that destroys superconductivity ($H^* \gtrsim H_c$ for $\varkappa < 0.417$, $H^* \gtrsim H_{c3}$ for $\varkappa > 0.417$); H_c is the critical field, and G is the Gibbs potential. The Ginzburg-Landau parameter, $\varkappa$, has been calculated only for type-II materials by the definitions

$$\varkappa_1 = \frac{H_{c2}}{\sqrt{2}}\, H_c\,, \tag{2}$$

and

$$\varkappa_2 = \left[0.5 + \frac{1}{8\pi\, 1.16\, (\partial M/\partial H)_{H_{c2}}}\right]^{1/2}. \tag{3}$$

We found experimentally no significant difference between $\varkappa_1$ and $\varkappa_2$, and we will write $\varkappa$ without an index in the following discussion.

The magnetostriction may be thermodynamically described by the differentiation of equation (1) with respect to a stress, σ, which is defined as a tension. Therefore $\partial G/\partial\sigma = -l$, where l is the length of the specimen. This yields

$$\frac{\Delta l}{l} = \frac{l_s(0) - l_n(H^*)}{l_s(0)} = \frac{1}{V}\frac{\partial V}{\partial\sigma}\frac{H_c^2}{8\pi} + \frac{\partial H_c}{\partial\sigma}\frac{H_c}{4\pi}\,. \tag{4}$$

The first term is a hydrostatic compression of the sample by the expelled magnetic field. It normally contributes less than 5 to 10%, but in In-25 at.% Pb, for example, this term contributes as much as 1/4 at 1.3 K. In previous works [1, 2] equation (4) is also given for intermediate H fields. In this case a third term in (4) appears for type-II materials. It is proportional to $\partial\varkappa/\partial\sigma$ and vanishes at H_{c2}. This third term is responsible for the increase of the dashed magnetostriction curve between H_{c1} and H_{c2}. It is also proportional to the amount of interface material present in the sample and has a maximum at the point where the distance between vortices is approximately two penetration depths, λ. At this point nearly the whole sample consists of interface material between normal regions at the center of the vortices and superconducting regions ($B \simeq 0$) between the vortices.

The stress dependence of $\varkappa$ can be simply deduced [1, 2] from the slope of the dashed magnetostriction and magnetization curves at H_{c2}

$$\partial \ln \varkappa / \partial \sigma = -\frac{1}{H_{c2}} \left. \frac{\partial \ln l / \partial H}{\partial M / \partial H} \right|_{H_{c2}} - \partial \ln H_c / \partial \sigma \,. \tag{5}$$

Temperature Variation

It is well known that $H_c(T)$ values can be fitted by

$$H_c(T) = H_0 \, f(t) \tag{6}$$

where $H_0 = H_c \; (T = 0)$, $t = T/T_c$ and $f(t)$ is usually approximated by a polynomial in t^2. By such a fit, H_0 and T_c can be deduced. It then follows using a formula given by Lock, Pippard and Shoenberg [11] that the Sommerfeld constant of the electronic specific heat is given by

$$\gamma = -V_m \, H_0^2 \, f''(0)/4 \, \pi \, T_c^2 \,, \tag{7}$$

where V_m is the molar volume and $f''(0) = d^2 f/dt^2 |_{t=0}$.

The magnetostriction experiments yield values of $\Delta l/l$ at different temperatures. These results are plotted in Figure 5. The curves are fits to the experimental points,

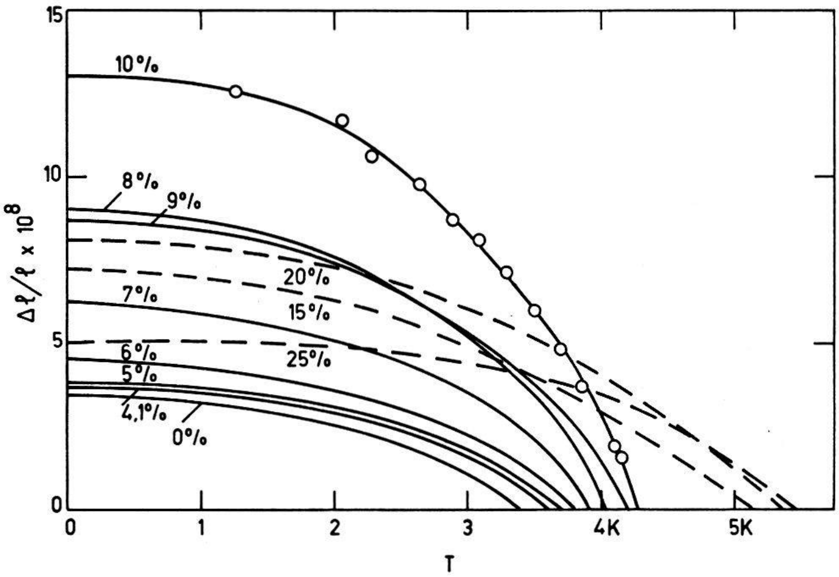

Figure 5
Total magnetostriction, $\Delta l(\mathrm{T})/l$, between zero field and normal state against the temperature, T, for the range of investigated alloys.

which are shown for the In-10 at.% Pb specimen. Statistical errors are $\sim 3 \times 10^{-9}$. Systematic errors are estimated to be of the order 10^{-8}, including possible deviations from the ideal polycrystalline structure or the nominal alloy mixture. These errors have been estimated by comparison of different samples (separately mixed and of different shape).

If $\partial \ln V/\partial\sigma$ and $H_c(T)$ are known, $\Delta l(T)/l$ yields $\partial H_c(T)/\partial\sigma$ by equation (4). In differentiating equation (6) with respect to σ one gets the expression

$$\partial H_c(T)/\partial\sigma = \partial H_0/\partial\sigma \cdot f(t) - \partial T_c/\partial\sigma \cdot H_0\, t\, f'(t)/T_c + H_0(\partial f/\partial\sigma)_t \tag{8}$$

to which the experimental $\partial H_c(T)/\partial\sigma$ values can be fitted having $\partial H_0/\partial\sigma$ and $\partial T_c/\partial\sigma$ as free parameters and $f(t)$ and H_0 deduced from (6). These quantities are further related to $\partial \ln \gamma/\partial\sigma$: One relation is found by differentiating (7) to give

$$\partial \ln \gamma/\partial\sigma = 2\,[\partial \ln H_0/\partial\sigma - \partial \ln T_c/\partial\sigma] + \partial \ln V/\partial\sigma + \partial \ln f''(0)/\partial\sigma\,. \tag{9}$$

A second relation follows a suggestion by Collins, Cowan and White [12]:

$$\partial \ln \gamma/\partial\sigma = \partial \ln\,[H_c^2(t_1) - H_c^2(t_2)]/\partial\sigma + \partial \ln V/\partial\sigma\,. \tag{10}$$

This is valid in the limit $t_1, t_2 \ll 1$, where the specific heat of the electrons can be neglected in the superconducting state.

$\partial \ln \varkappa(T)/\partial\sigma$ we have found to be approximately independent of T.

Special Assumptions

The specimens are assumed to be ideally polycrystalline, which leads to $\partial \ln V/\partial\sigma = -1/3\ \partial \ln V/\partial p$ (assumption 2), where p is a hydrostatic pressure. Since no measurements of the elastic constants of In-Pb alloys were available we used the pure indium value of Anderson [13] $\partial \ln V/\partial\sigma = 7.2\times 10^{-13}$ cm^2/dyn at $T = 0$ (assumption 3). This value is used to calculate the volume dependence of the thermodynamic parameters from the stress derivatives.

We also must choose an expansion of the function $f(t)$. This is usually written

$$f(t) = 1 + \sum_{n=1}^{\infty} c_n\, t^{2n} \quad \text{with} \quad f(1) = 0\,. \tag{11}$$

We used this form of $f(t)$ but we realized that it converges very badly. This is a disadvantage, particularly when f is to be differentiated with respect to a stress. A better expansion of $f(t)$ could possibly be obtained on the basis of a scaled energy gap parameter, Δ, and the BCS-theory. Finnemore and Mapother [14] fitted in this way $H_c(T)$ values of pure metals. For alloys such fits should be even better, because, as shown by Anderson [15], an averaged gap rather than the real anisotropic gap is responsible for the superconductivity. The advantage of the proposed fit to $f(t)$ would be that the derivative $\partial\Delta/\partial\sigma$ makes more physical sense than $\partial c/\partial\sigma$ in the differentiation of (11).

Unfortunately our $H_c(T)$ measurements did not include temperatures lower than 1.25 K and were not very accurate. Therefore we decided to follow the conventional expansion (11) and assumed that

$$(\partial f/\partial\sigma)_t = 0\,, \qquad \text{(assumption 4)}$$

which implies that $\partial f''(0)/\partial\sigma = 0$. For f we have chosen

$$f(t) = 1 + c_1\, t^2 + c_2\, t^4\,. \qquad \text{(assumption 5)}$$

To satisfy the condition $f(1) = 0$ we write

$$f(t) = 1 - (1 + a)\, t^2 + a\, t^4 \,. \tag{12}$$

The constant c_1 is 1.07 for pure indium after Berman, Brandt and Ginzburg [16] and nearly pressure independent. This yields $a = 0.07$. By fitting our data to equation (12) we found $a \simeq 0.1$ for all indium alloys with less than 4 at.% Pb (type-I superconductors). For type-II materials 'a' scattered statistically from run to run and sample; but the mean value was still ~ 0.1. We have therefore chosen the value $a = 0.1$ (assumption 6) for all In-Pb measurements.

Thermodynamic Properties

The thermodynamic parameters deduced from the equations given above and using the assumptions mentioned are plotted against the lead content in Figures 6 and 7.

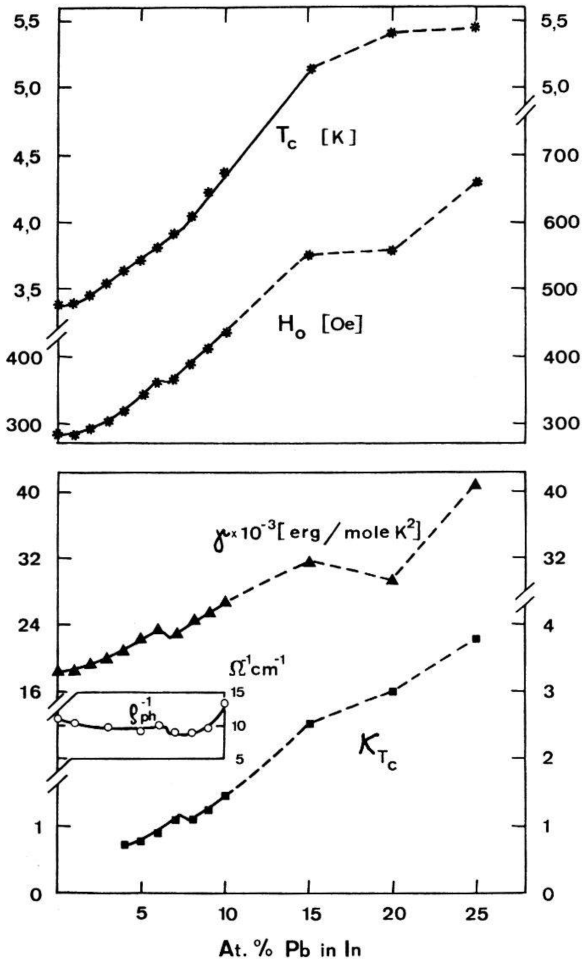

Figure 6
Parameters deduced from magnetization measurements and directly measured values of ϱ_{ph}.

The comparison with other measurements gives the following:

Figure 6: Gygax [5] has measured T_c, H_0, γ and $\varkappa_{T_c}$ values in In with 0 to 10 at.% Pb. Our T_c, H_0 and $\varkappa$ values agree well with his, but our γ values are systematically larger because of a larger f'' used in assumption 1. Merriam [3] has found

a linear increase in T_c from 7 to 15 at.% Pb. We have therefore drawn a full line in this region. According to a suggestion by Andres [17], we also measured the reciprocal of the electrical resistivity due to the phonon scattering, ϱ_{ph}^{-1}. This should have a similar dependence on the lead content as γ because both parameters are proportional to the electron density of states at the Fermi surface and because the mass enhancement constant, λ, which enters γ as a factor $1 + \lambda$ is related to ϱ_{ph}^{-1}. We have therefore measured the resistivity at room temperature and subtracted the residual part using Gygax's values. The reciprocal of the difference, ϱ_{ph}^{-1}, is plotted in Figure 6 below the γ curve.

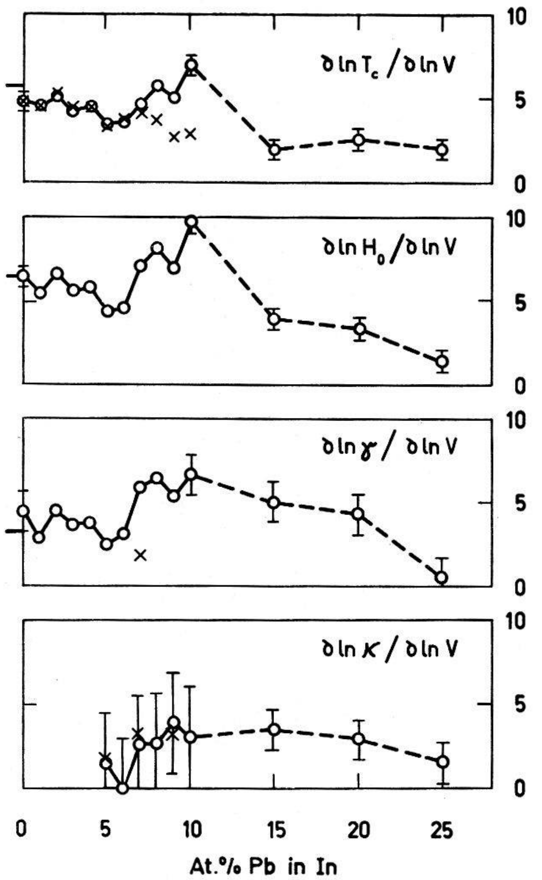

Figure 7
Parameters deduced from magnetostriction measurements.

Figure 7: In pure indium Collins, Cowan and White [12] have measured values that are given by thick strokes on the left side of the figure. The crosses are measurements by Fischer [18]. He cast his specimens from the same alloys as we. Fischer's and our values of $\partial \ln T_c / \partial \ln V$ are in good agreement from 0 up to 7 at.% Pb. The disagreement for the higher lead contents, which is far beyond the estimated errors, may be due to the invalidity of assumptions 4, 5 and 6 in these alloys. These alloys are stronger coupled superconductors than pure indium as was found recently by one of us (G. B.) on measuring the energy gap, Δ, of In-10 at.% Pb by the absorption of far infra red radiation. For $2\Delta(0)/k\,T_c$ resulted a value of 3.9 ± 0.15 which is significantly higher than 3.69 ± 0.04 reported for indium by Norman [19].

Discussion

In this section we discuss the results in relation to changes in the Fermi surface. Related work has recently been done for indium rich alloys with thallium (White and McCollum [20]) and cadmium (Higgins and Kaehn [21]).

Measurements of the crystalline structure by Moore, Graham, Williamson and Raynor [8] are described in the introduction. From their data one can further deduce the atomic volume, which is found to increase by 5% from 0 to 25 at.% Pb in In. This is roughly a factor 4 too small a volume change to explain the very big increase in T_c, H_0, γ and K_{T_c} depicted in Figure 6 by multiplying the parameters of Figure 7 with ΔV. This has two consequences: 1. The curves in Figure 7 are not the differentiated curves of Figure 6, although they nearly appear to be, and 2. there must result large changes of the Fermi surface and the mass enhancement constant, λ, due to the lead admixture.

Ashcroft and Lawrence [22] find the following picture of the Fermi surface of pure indium: The first zone is filled, the second zone is singly connected and contains electron holes. The monster of the third zone as it is found in aluminium (cubic structure) is reduced to rings, the β-arms, and to small pockets, the α-arms, by the tetragonal distortion of the indium crystal lattice. The α-arms are probably not occupied. By the admixture of lead the tetragonal distortion increases until 7 at.% Pb, where the ratio of the lattice constants, c/a, has a maximum. We suppose this to be due to an increase in the β-arms. At 7 at.% Pb the α-arms begin to fill up. At 13 at.% Pb c/a jumps from $c/a > 1$ to $c/a < 1$. This has been explained by pseudo-potential methods by Heine and Weaire [23]. Above 13 at.% Pb the α-arms which are two times more frequent are occupied and the β-arms empty. We suppose that when lead is further added the α-arms increase (analogously to the β-arms for 0 to 7 at.% Pb) until the minimum in c/a at $\sim$20 at.% Pb is reached.

On comparing the increase in $\gamma = N(0)\,(1 + \lambda)$ due to the lead admixture (Fig. 6) with the calculations of the density of states, N, by Ashcroft and Lawrence [22] in their Figure 13, and assuming that each lead atom brings one extra electron, we have to conclude that λ increases appreciably starting near 0.7 for pure indium.

It is surprising that the phase change at 13 at.% Pb has a small influence on the parameters plotted in Figure 6, whereas the maximum and minimum in c/a at 7 at.% Pb are clearly detectable. $\partial \ln T_c/\partial \ln V$ and $\partial \ln H_0/\partial \ln V$ values in Figure 7 show, however, a step at 13 at.% Pb.

Remarkable in this context are also the X-ray measurements by Raynor and Graham [24], who have studied indium containing 0 to 25 at.% Pb with a constant admixture of 5 at.% Tl. If one assumes that the main contribution of Tl is an increase in the volume of the alloys and that the number of conduction electrons per atom is not changed, one finds that $\partial \ln(c/a)/\partial \ln V$ for In-Pb alloys is ranging between -1.5 and -3.0. This shows again that the axial ratio c/a is an important parameter in the discussion of measurements on indium-lead alloys of tetragonal crystal structure.

Conclusions

We have shown that in In alloys with 0 to 25 at.% Pb strong variations in the magnetostriction, both in the absolute value and in the shape of the curves, are detectable. In particular, the sign change of the magnetostriction in increasing field for indium with 20 and 25 at.% Pb is remarkable. The data from the magnetization measurements also shows strong variations due to the lead admixture: T_c, H_0 and γ increase by ~100%. These effects, we found, are related to changes in the Fermi surface, the crystal structure, and the mass enhancement constant.

Acknowledgments

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REFERENCES

[1] G. Brändli and F. D. Enck, Phys. Lett. *26 A*, 360 (1968); erratum, *27 A*, No. 1 (1968).
[2] G. Brändli, Phys. Kondens. Mat. *11*, 93 and 111 (1970).
[3] M. F. Merriam, Phys. Rev. Lett. *11*, 321 (1963).
[4] W. Meissner, N. Franz and H. Westerhoff, Ann. Phys. *13*, 505 (1962).
[5] S. Gygax, Phys. Kondens. Mat. *4*, 207 (1965).
[6] K. Noto, Y. Muto and T. Fukuroi, J. Phys. Soc. Jap. *21*, 2122 (1966).
[7] C. Tysack and G. V. Raynor, Trans. Faraday Soc. *50*, 675 (1954.)
[8] A. Moore, J. Graham, G. K. Williamson and G. V. Raynor, Acta Metallurgica *3*, 579 (1955).
[9] M. F. Merriam, Rev. Mod. Phys. *36*, 152 (1964).
[10] G. Brändli, F. D. Enck, E. Fischer and R. Griessen, Proc. XI. internat. Conf. Low Temp. Phys., St. Andrews 1968, Vol. 2 (Univ. Press., 1968), p. 969.
[11] J. M. Lock, A. B. Pippard and D. Shoenberg, Proc. Cambridge Phil. Soc. *47*, 811 (1951).
[12] J. G. Collins, J. A. Cowan and G. K. White, Cryogenics *7*, 219 (1967).
[13] O. L. Anderson, in W. P. Mason, *Physical Acoustics*, Vol. III B (Academic Press, New York 1965), p. 88.
[14] D. K. Finnemore and D. E. Mapother, Phys. Rev. *140*, 507 (1965).
[15] P. W. Anderson, J. Phys. Chem. Solids *11*, 26 (1959).
[16] I. V. Berman, N. B. Brandt and N. I. Ginzburg, Zh. Eksp. i Teor. Fiz. *53*, 124 (1967); engl. Transl: Soviet Phys. JETP *26*, 86 (1968).
[17] K. Andres, private communication.
[18] E. Fischer, Helv. phys. Acta *42*, 1003 and 1022 (1969).
[19] S. L. Norman, Phys. Rev. *167*, 393 (1968).
[20] H. W. White and D. C. McCollum, Phys. Rev. B, *1*, 552 (1970).
[21] R. J. Higgins and H. D. Kaehn, Phys. Rev. *182*, 649 (1969).
[22] N. W. Ashcroft and W. E. Lawrence, Phys. Rev. *175*, 938 (1968).
[23] V. Heine and D. Weaire, Phys. Rev. *152*, 603 (1966).
[24] G. V. Raynor and J. Graham, Trans, Faraday Soc. *54*, 161 (1958).