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The Discovery of Type II Superconductors (Shubnikov Phase)

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"It is a fascinating testament to Shubnikov's great originality and to the terrible times that deprived him of his life and we all of the fruits of the science for so long. Even now, many do not really understand the breakthrough made in Kharkov."
From the letter of 31 December, 2008, written by Shubnikov Professor D. Larbalistier, Director of Applied Superconductivity Center, USA, on reprinting in English the article (Shubnikov et al., 1937) in 2008.

1. Introduction

At present, Type II superconductors enjoy wide applications in science and technology. It is worth noting that all the superconductors, from Nb_3Sn to cuprates, fullerenes, MgB_2, iron-based systems that have been discovered for the last 50 years, are Type II superconductors. It is of interest to trace back the intricate research carried out for 8 years from 1929 (De Haas & Voogd, 1929) to 1936 by experimenters in four countries out of the five, who had liquid helium at their laboratories at the time when L.V.Shubnikov, V.I.Khotkevich, G.D.Shepelev, Yu.N.Ryabinin (Schubnikow et al., 1936; Shubnikov et al., 1937; Shepelev, 1938) discovered experimentally in Kharkov the phenomenon of Type II superconductivity in single-crystal, single-phase superconducting alloys. A theoretical explanation of the phenomenon, based on experimental results (Shubnikov et al., 1937) and the Ginzburg-Landau theory (Ginzburg & Landau, 1950; Ginzburg, 1955), was given by A.A.Abrikosov only in 1957 (Abrikosov, 1957). The proposed publication lays out the recognition of the discovery of Type II superconductors by leading specialists in this area and indicates a role which this phenomenon plays in the science and technology. Unfortunately, neither L.D.Landau nor anyone of the pioneer-experimenters lived to witness the awarding the corresponding Nobel Prize 2003 when it was given to V.L.Ginzburg and A.A.Abrikosov.

All the superconductors are known to be of two types depending on the magnitude of the ratio:

$$æ = \lambda / \xi ,$$

where æ – the Ginzburg-Landau parameter, λ - the penetration depth of magnetic field, ξ – the coherence length between electrons in Cooper pair (Fig.1). For the typical pure superconductors $\lambda \sim 500$ Å, $\xi \sim 3000$ Å, i.e. æ<<1. A critical value used to determine the superconductor type is the following: $æ_c = 1/\sqrt{2}$ (Ginzburg & Landau, 1950; Ginzburg, 1955).
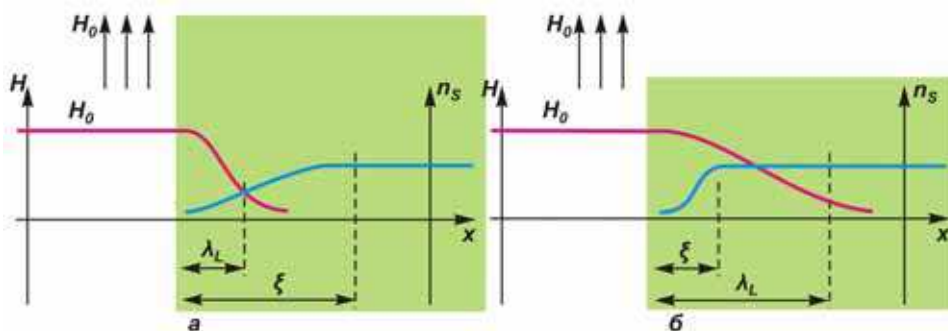
Fig. 1. Schematic diagram of interface between normal and superconducting phases: a) Type I superconductor; b) Type II superconductor. n_s – density of superconducting electrons (After Ginzburg & Andryushin, 2006).

Magnetic properties of these two superconductor types are essentially different (Fig.2). This phenomenon can be attributed to the fact that in the *Type I superconductors* (pure superconductors), where the Ginzburg-Landau parameter $\text{æ} < 1/\sqrt{2}$ (Ginzburg & Landau, 1950; Ginzburg, 1955), the n-s interphase surface energy $\sigma_{ns} > 0$. For this reason, under the impact of magnetic field an intermediate state, as shown by L.D.Landau (Landau, 1937; Landau, 1943), is created in those superconductors of arbitrary shape (with the demagnetizing factor $n \neq 0$) where the layers of the normal and superconducting phases alternate.
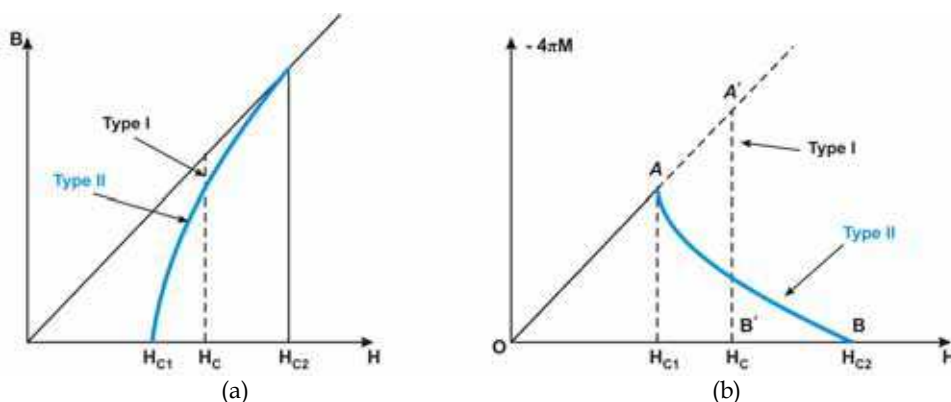

Fig. 2. (a) The induction in the long cylinder as a function of the applied field for Type I and Type II superconductors; (b) The reversible magnetization curve of a long cylinder of Type I and Type II superconductor (After De Gennes, 1966)

In *Type II superconductors* (superconducting alloys), where $\text{æ} > 1/\sqrt{2}$, the n-s interphase surface energy $\sigma_{ns} < 0$ and magnetic field penetrates these superconductors in the form of the Abrikosov vortex lattice (Abrikosov, 1957). As indicated by A.A.Abrikosov (Abrikosov, 1957), the idea about the alloys turning into Type II superconductors at the value of the parameter $\text{æ} > 1/\sqrt{2}$ was first brought forward by L.D.Landau.

Yet, it took about 30 years since the pioneering experimental research on superconducting alloys under applied magnetic field to understand fully the Type II superconductivity phenomenon.

The theory of Type II superconductors has been expounded in detail over the past 45 years in scores of reviews and monographs on superconductivity, the experimental side of the discovery of these superconductors, as far as the author knows, having been discussed only fragmentarily either at the early stages of the research (Burton, 1934; Wilson, 1937; Ruhemann, 1937; Shoenberg, 1938; Jackson, 1940; Burton et al., 1940; Ginzburg, 1946; Mendelssohn, 1946; Shoenberg, 1952) or later on (refer to the authoritative published papers (Mendelssohn, 1964; Mendelssohn, 1966; Goodman, 1966; De Gennes, 1966; Saint-James et al., 1969; Anderson, 1969; Chandrasekhar, 1969; Serin, 1969; Hulm & Matthias, 1980; Hulm et al., 1981; Pippart, 1987; Berlincourt, 1987; Dahl, 1992[1]; Dew-Hughes, 2001) and also to (Sharma & Sen, 2006; Slezov & Shepelev, 2008; Karnaukhov & Shepelev, 2008, Slezov & Shepelev, 2009)). Therefore, the way the real events took place is, quite regrettably, largely hidden from view to many of the International Scientific Community.

We shall remind that H.Kamerlingh Onnes (Physical Laboratory, University of Leiden), an outstanding physicist of those times, who discovered the phenomenon of superconductivity in *pure metals* in 1911 (Kamerlingh Onnes, 1911), was the first with his co-workers to take an interest beginning from 1914 in the effects of magnetic field on those superconductors (Kamerlingh Onnes, 1914; Tuyn & Kamerlingh Onnes, 1926; Sizoo et al., 1926; De Haas et al., 1926, De Haas & Voogd, 1931a). In particular, it was found that superconductivity in pure metals got suddenly disrupted when impacted by an applied magnetic field with a critical value H_c (in the case of the demagnetizing factor n = 0), which manifested itself in a sudden restoration of electrical resistance of the samples from zero to such value that corresponded to T>T_c (Fig.3).
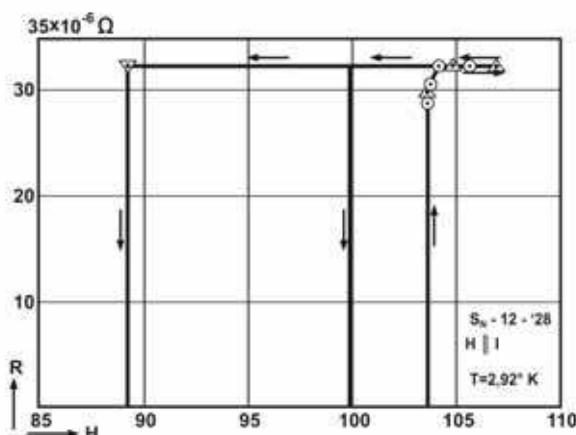

Fig. 3. Sudden change of electrical resistance of wire sample of single crystal tin at T<T_c, as caused by longitudinal magnetic field (After De Haas & Voogd, 1931a).

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[1] In the interesting book, Dahl (Dahl, 1992) has erroneously ascribed the discovery of Type II superconductors to some other article from Kharkov. In reality, as is well known (see 4. Recognition), the world's leading specialists in superconductivity unanimously relate this discovery to the articles by L.V.Shubnikov V.I.Khotkevich, G.D.Shepelev, Yu.N.Ryabinin. (Schubnikow et al., 1936, Shubnikov et al., 1937).

It should be said that, aside from the feature of *electric properties* of Type I superconductors upon decreasing temperature below T_c (the steep fall of electrical resistance down to such resistivity which was smaller than 10^{-23} $\Omega \cdot cm$), the second fundamental characteristic of pure superconductors (*magnetic properties)* also had a peculiarity that was out of the ordinary. In 1933 W. Meissner and R. Ochsenfeld (Physikalische Technische Reichsanstalt) found (Meissner & Ochsenfeld, 1933) that a magnetic field which was smaller than H_c did not run through a *pure superconductor*, the magnetic induction in it being B = 0 (with the exception of a very thin surface layer ~ λ). Under the impact of an applied magnetic field with the value H_c the pure superconductor magnetization M and induction B also changed with a jump (Fig.4). These values are related via the following ratio:

$$M = (B - H) / 4\pi.$$

The exclusion of flux from the bulk of pure superconductor is called the Meissner effect.
Any discovery is generally preceded by a preparatory period. Then, some day or other, following the actual discovery the recognition is accorded. Some time after that one can look at final results and evaluate the prospects.

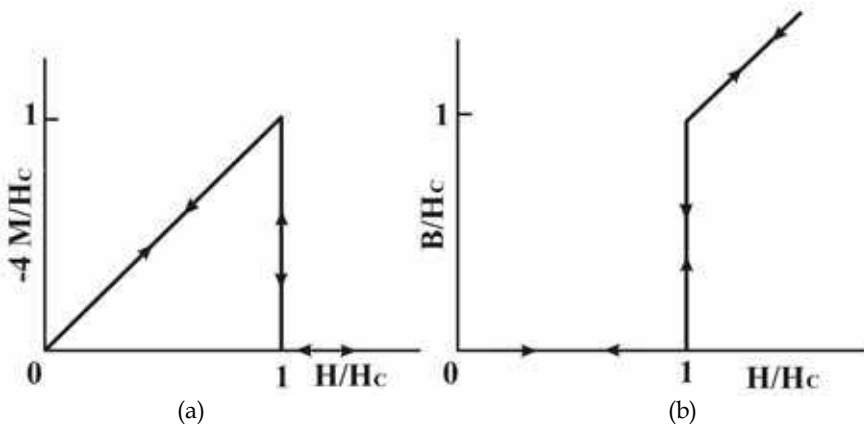(a)   (b)

Fig. 4. a) Magnetization curve of a pure superconducting long cylinder in longitudinal magnetic field; b) B-H curve of a pure superconducting long cylinder in longitudinal magnetic field (After Shoenberg, 1938).

2. Preliminary stage

Interestingly enough, even before the Meissner effect was discovered, W.J.De Haas, J.Voogd (Kamerlingh Onnes Laboratory, University of Leiden) had discovered (De Haas & Voogd, 1929) a distinction between the behavior in applied magnetic field of *electrical resistance* of polycrystals of *superconducting alloys* and that of pure superconductors. It appeared that in rod specimens of the alloys Bi + 37.5at%Tl, Sn + 58wt%Bi, Sn +28.1wt%Cd (the latter two being close to the eutectic alloy) (De Haas & Voogd, 1929), in the alloy Pb + 66.7at%Tl, the eutectic Pb + Bi and in the alloys Pb-Bi (7wt%; 10wt%; 20wt%), Sn + 40.2wt%Sb (De Haas & Voogd, 1930), in the alloys Pb + 15wt%Hg, Pb + 40wt%Tl, Pb + 35wt%Bi, the eutectic Au-Bi (De Haas & Voogd, 1931b) the disruption of superconductivity occurred across a broad interval of magnetic fields irrespective of the orientation of the field running parallel, i.e. at

n=0 (Fig.5), or perpendicular (Fig.6) to the axis of cylindrical specimens, i.e. at n = ½ [2]). As D.Shoenberg noted (Shoenberg, 1938; Shoenberg, 1952), for superconducting alloys "*there is much less difference between the curves for a transverse and a parallel field than there is for a pure superconductor*".
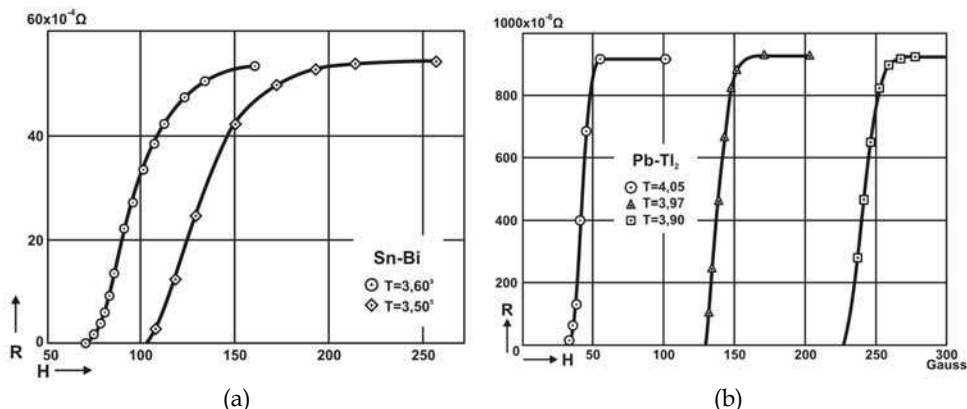

(a)　　　　　　　　　　　　　　　　(b)

Fig. 5. The resistance of superconducting long cylinder for polycrystalline Sn-Bi alloy (After De Haas & Voogd, 1929) and Pb-Tl alloy in longitudinal magnetic field (After De Haas & Voogd, 1930).
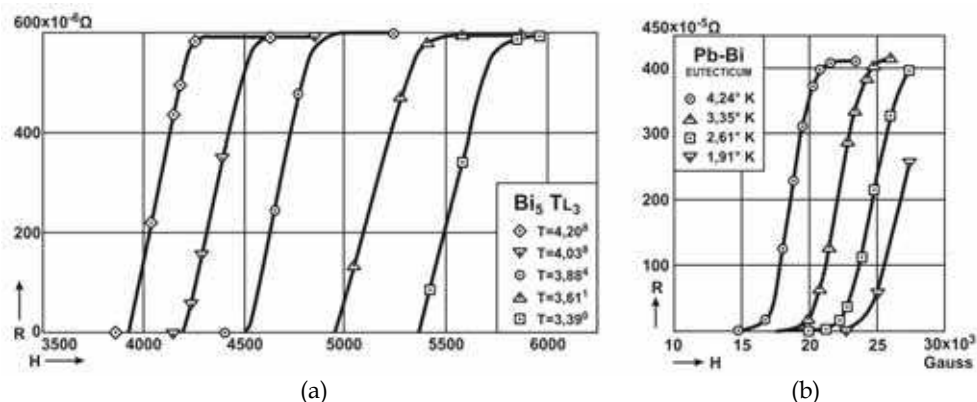

(a)　　　　　　　　　　　　　　　　(b)

Fig. 6. Variation of electrical resistance of cylindrical specimens of superconducting alloys Bi-Tl (After De Haas & Voogd, 1929), Pb-Bi (After De Haas & Voogd, 1930) in transverse magnetic field at various temperatures.

During studies on the electric properties of the eutectic Pb-Bi, while decreasing applied magnetic field from H_c to zero, (De Haas & Voogd, 1930) found a clear-cut hysteresis about

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[2] The exact data about the composition of research alloy samples are given: for alloys Sn-Bi, Sn-Cd, Pb-Bi in (De Haas et al., 1929a), Pb-Tl in (De Haas et al., 1930), Sn-Sb in (Van Aubel et al., 1929), Au-Bi in (De Haas et al., 1929b).

which many authors wrote later so very many scientific papers. Much later, it was shown (Saint-James & DeGennes, 1963) that in the case of the magnetic field that ran parallel to the surface in the interval $H_{c2} < H < H_{c3} = 1,695H_{c2}$ a superconducting layer of the thickness on the order of ξ was formed on the surface of the sample. The problems of the hysteresis and "frozen-in" magnetic flux in such superconducting alloys that, as established later on, were strongly dependent on sample quality (compositional inhomogeneities, impurities, stresses) were discussed in minute detail in monographs by D.Shoenberg (Shoenberg, 1938; Shoenberg, 1952).

W.J.De Haas, J.Voogd noted quite reasonably (De Haas & Voogd, 1929), that the eutectic research samples were a mixture of two phases, one of which shunted the entire sample when the electrical resistance was taken. The difference in the disruption of superconductivity of the alloys, for instance Pb +66.7at% Tl and Pb +40wt% Tl, relative to pure superconductors was attributed by the above authors to the possible influence from inhomogeneities in the alloy samples (De Haas & Voogd, 1930; De Haas & Voogd, 1931b).

Unfortunately, in the early 20th century not all of the phase diagrams of the alloys were known precisely. According to data from such a prestigious source as (Massalski, 1987) (Fig.7 and 8) the majority of the alloys studied by W.J.De Haas, J.Voogd (De Haas & Voogd,
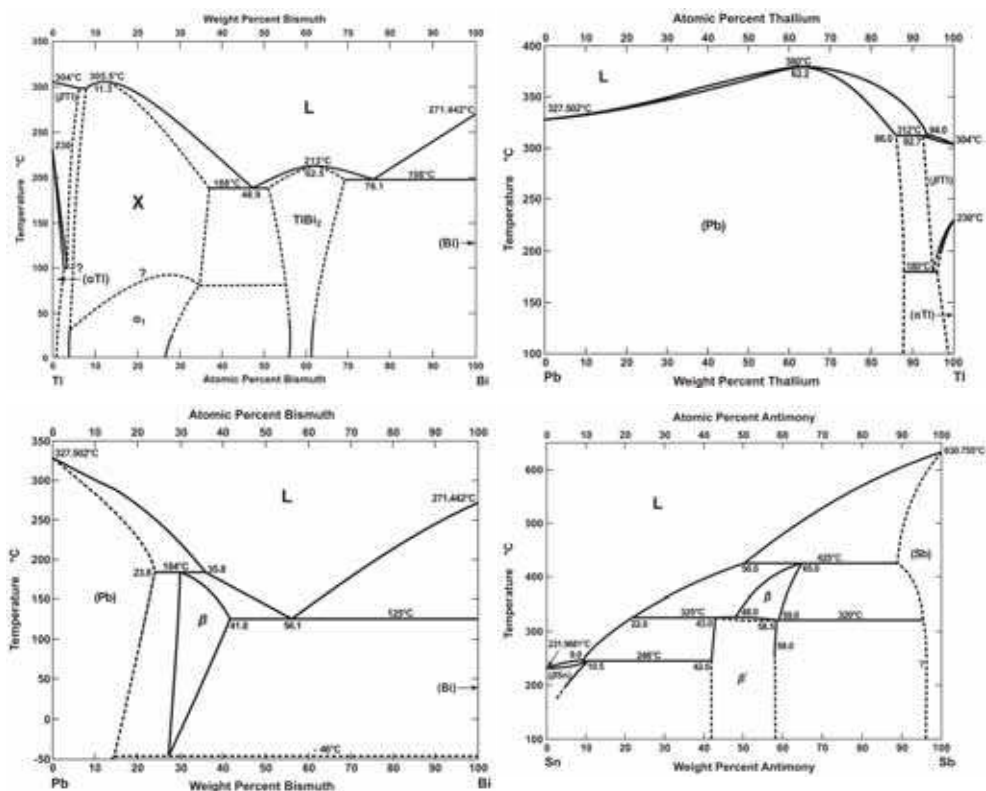

Fig. 7. Binary phase diagrams of the alloys Tl-Bi, Pb-Tl, Pb-Bi, Sn-Sb (After Massalski, 1987).
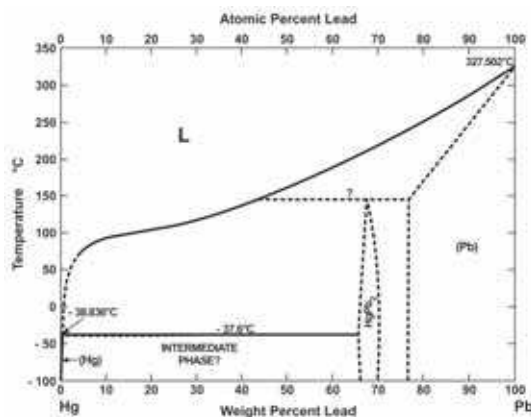
Fig. 8. Binary phase diagrams of the alloy Hg-Pb (After Massalski, 1987).

1929; De Haas & Voogd, 1930; De Haas & Voogd, 1931b) (except the alloys Pb+Tl, Pb+Bi (7wt%; 10wt%) and Pb+15wt%Hg) had more than one phase, i.e. they were distinctly inhomogeneous as were the alloys with the eutectics Sn-Bi, Sn-Cd, Pb-Bi, Au-Bi.

The discovery in the eutectic Pb-Bi of preservation of superconductivity under applied fields on the order of 2T allowed W.J.De Haas, J.Voogd (De Haas & Voogd, 1930) to bring back to life a dream that had been cherished by H.Kamerlingh Onnes about creating magnetic fields by using superconducting solenoids without wasting much energy. However, neither in Kharkov, nor in Leiden, nor in Oxford this dream was not to come true on account of the low value of the current that acted to disrupt the superconductivity (Rjabinin &Schubnikow, 1935a; Keesom, 1935; Mendelssohn, 1966). Thirty years on, K.Mendelssohn (Mendelssohn, 1964; Mendelssohn, 1966) reasoned that the resolution of this challenge, as it were, called for a change in mentality, a heretofore inconceivable progress in scientific engineering and scope of scientific research, as well as for considerable increases in the funding of the Science.

The subsequent experimental research indicated that not only the behavior of the electrical properties, but also that of the *magnetic ones*, in superconducting alloys were different to the properties of the pure superconductors. In the span of *1934-1936* there was a thrilling "*hurdle race*" in the studies on magnetic properties of superconducting alloys between scientists of four countries out of the five that had liquid helium at their laboratories at that moment. Considering that the superconductors possessed a large magnetic moment, the methods used in the works below were based on the standard magnetic measurements. Using a fluxmeter or a ballistic galvanometer, the measurements were made of magnetization-vs.-voltage characteristics in the coil that surrounded the sample: during sample cooling in constant pre-assigned magnetic field or after sample pulling out of the coil at constant temperatures and magnetic fields, or upon turning on and off the constant magnetic field, or during stepping up or down the magnetic field little-by-little across the entire range from zero to H_c and back.

Canadian scientists F.G.A.Tarr and J.O.Wilhelm (McLennan Laboratory, University of Toronto) submitted a paper for publication (Tarr & Wilhelm, 1935) *on September 14, 1934* which contained the results of their studies on magnetic properties of superconducting mercury, tin, tantalum, as well as the alloys with the eutectic Pb+Sn (40wt%; 63wt%; 80wt%) and the multiphase alloy Bi+27.1wt% Pb+22.9wt%Sn, observable under the impact of applied magnetic field. Fig.9 presents the phase diagram of the ternary alloy. In particular, a
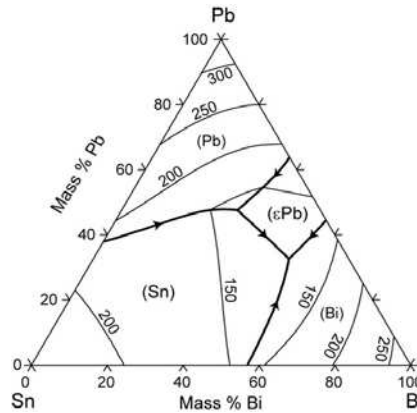
Fig. 9. Phase diagram of the alloy Bi-Pb-Sn (After Kattner, 2003).

study was made on decreasing the magnetic flux running through plane disklike samples during their cooling at a constant magnetic field which was perpendicular to the disk plane (n=1) from a temperature higher than T_c to the temperature corresponding to H_c. Whereas the magnetic flux was completely expelled from the pure mercury sample, in samples of the commercially produced tin, lead, tantalum (evidently of insufficient purity) the "frozen-in flux" was observable. There was no Meissner effect in the alloys that had more than one phase Pb+Sn (40wt%; 63wt%; 80wt%) and Bi+27.1wt% Pb+22.9wt%Sn at all.

T.C.Keeley, K.Mendelssohn, J.R.Moore (Clarendon Laboratory, Oxford University) in their paper (Keeley et al., 1934) submitted for publication on *October 26, 1934* and published on *November 17* of the same year presented the results of induction measurements in long cylindrical specimens of mercury, tin, lead and alloys Pb+Bi (1wt%; 4wt%; 20wt%), Sn+28wt%Cd, Sn+58wt%Bi (pre-cooled to a temperature below T_c) upon turning on and then off the longitudinal magnetic field (n = 0). It appeared that the "frozen in" magnetic flux, remaining in the sample («frozen in» induction) was zero for pure mercury, but a *"small addition of another substance has the effect of "freezing in" the entire flux which the rod contains at the Hc, when the external field is switched off"*. The authors reported that at a temperature below T_c in samples of the said-alloys in longitudinal magnetic field *"it was observed in most cases that the change of induction did not seem to take place at a definite field strength but, at a constant temperature, extended over a field interval, amounting to 10-20 per cent of the threshold value field"*. Let us say that a greater portion of the alloy compositions studied by these authors had been earlier investigated by W.J.De Haas, J.Voogd (De Haas & Voogd, 1929; De Haas & Voogd, 1930; De Haas & Voogd, 1931b); the single-phase alloys being only Pb+Bi (1wt%; 4wt%).

On December 22, 1934 in their report at a session of Royal Academy (Amsterdam) W.J.De Haas and J.M.Casimir-Jonker (De Haas & Casimir-Jonker, 1935a) reported the results of studies on magnetic properties of carefully prepared polycrystals of alloys Bi+37.5at.%Tl (multiphase alloy) and Pb+64.8wt%Tl. The samples were cylinders 35 mm long, 5 mm in diameter, with a narrow 1 mm dia. duct running along the axis; the applied magnetic field was incident perpendicular to the axis of the cylinders (n = ½). The measurement of the magnetic field inside the samples was made over measurement of the electrical resistance of a miniature bismuth wire placed in the middle of the duct. Apparently, for both alloys at temperatures below T_c the magnetic field began to penetrate the superconducting alloys only after attaining a certain value of the applied field (Fig.10).

In this way, it turned out that there were three characteristic fields in the superconducting alloy: a weak field of the incipient penetration of the magnetic flux into the alloy, a field of the onset of a gradual restoration of electrical resistance and a field of the complete transition of the alloy into the normal state (Fig.11). Articles covering those studies were submitted by W.J.De Haas and J.M.Casimir-Jonker on *December 7, 1934* to the prestigious "Nature" (which ran it on *January 5, 1935 (*De Haas & Casimir-Jonker, 1935b)) and to the sole low-temperature physics dedicated authority of those times "Communications from the Physical Laboratory of the University of Leiden» (De Haas & Casimir-Jonker, 1935c) (refer also to the paper (Casimir-Jonker & De Haas, 1935) submitted for publication on *July 29, 1935).*

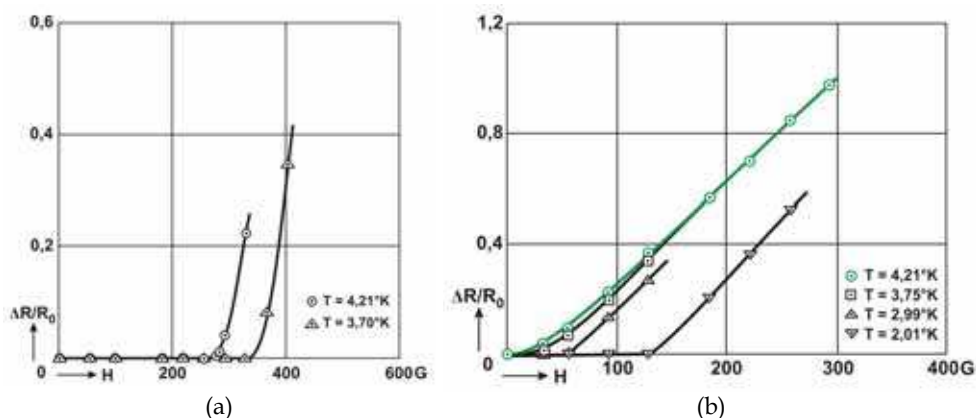(a)   (b)

Fig. 10. Penetration of magnetic field into the superconducting alloys Bi+37,5at.%Tl (left) and Pb+64,8wt%Tl (right). For alloy Pb+64,8wt%Tl curve at 4,21 K obtained for normal state (T>T_c) (After De Haas & Casimir-Jonker, 1935c).
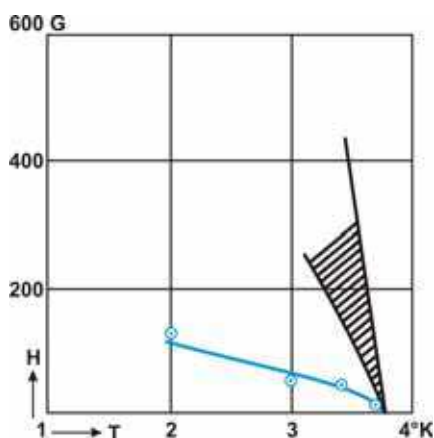

Fig. 11. Temperature dependence of the incipient penetration of magnetic field into the superconducting alloy Pb+64.8wt%Tl. The hatched region denotes the region of gradual flux penetration in magnetic field according to the electrical resistance measurement data (After De Haas & Casimir-Jonker, 1935a).

Fig. 12. Cryogenic Laboratory's Researchers, 1933. From left to right: (the first line)
N.S.Rudenko (second), N.M.Zinn (third), O.N.Trapeznikova (fourth), Yu.N.Ryabinin (fifth),
A.I.Sudovtsov (sixth), Dogadin (seventh); (the second line) G.D.Shepelev (third),
L.V.Shubnikov (fourth), I.P.Korolyov (fifth), V.I.Khotkevich (sixth), V.A.Maslov (ninth).

L.V. Shubnikov, who was known to be working very successfully with W.J.De Haas from
autumn of 1926 until summer of 1930 at Kamerlingh Onnes Laboratory (it was there exactly
that the Shubnikov–De Haas Effect – the periodic magnetoresistance oscillations in pure
metal at low temperatures – was discovered), knew well about his research into
superconducting alloys. Having created at Ukrainian Physical-Technical Institute (UPhTI,
now the National Science Center «Kharkov Institute of Physics and Technology» - NSC
KIPT) the first Cryogenic Lab in the USSR (Fig.12), in 1934 he went into that research, too.
In paper submitted for publication on *January 27, 1935* (Rjabinin & Schubnikow, 1935a) (its
summary published by the "Nature" on *April 13, 1935* (Rjabinin & Schubnikow, 1935b))
Yu.N. Ryabinin and L.V.Shubnikov supported the existence of the incipient penetration
field (Fig.13) in a single crystal of the superconducting alloy Pb + 66.7at.%Tl and in the
multiphase polycrystal Pb-35wt%Bi (samples of those alloys had been studied earlier by
W.J.De Haas, J.Voogd (De Haas & Voogd, 1930; De Haas & Voogd, 1931b)) and designated it
correspondingly as H_{c1}. It was confirmed that prior to the field H_{c1} there was the magnetic
induction B=0 in the alloy Pb + 66.7at.%Tl, while in the interval of field strengths from H_{c1} to
the field of total superconductivity disruption, which was designated by them as H_{c2}, the
induction gradually increased with increasing applied field. The authors also measured the
temperature relationship of H_{c1}, H_{c2} and field of critical current H_{cj} which acted to disrupt
the superconductivity (Fig.14). It is noteworthy that Yu.N.Ryabinin and L.V.Shubnikov, as
had done earlier W.J.De Hass and J.Voogd (Haas & Voogd, 1930; Haas & Voogd, 1931b), did
not rule out a possibility that "*unusual behavior of alloys is caused by their inhomogeneity which
may be due to the decomposition of the solid solution and the formation of a new very disperse phase*"
(Rjabinin & Schubnikow, 1935a).

On *April 3, 1935* K. Mendelssohn and J.R.Moore (Mendelssohn & Moore, 1935) submitted a new article (published on *May 18, 1935)* in which they supported the existence of the incipient field of penetration into the multiphase alloy Pb+70wt%Bi. The article put forward a hypothesis about a "Mendelssohn Sponge" that suggested the existence in superconducting alloys of inhomogeneities of the composition, structure and internal stresses such that caused the formation of multiple-connection thin structures with anomalously high critical fields serving as current paths (for more detail, refer to the Mendelssohn report on *May 30, 1935,* in Discussion on Superconductivity and Other Low-Temperature Phenomena at Royal Society (London) (Mendelssohn, 1935), where he indicated *"that the amount of "frozen in" flux depended mainly on the purity, lead with 1%, 4%, 10% bismuth was investigated, and the results actually showed that the "frozen in" increased with the addition of the second component."*). Nonetheless, the existence of the Mendelssohn Sponge could not account for the magnetic field penetration at $H < H_c$ in Type II superconductors.
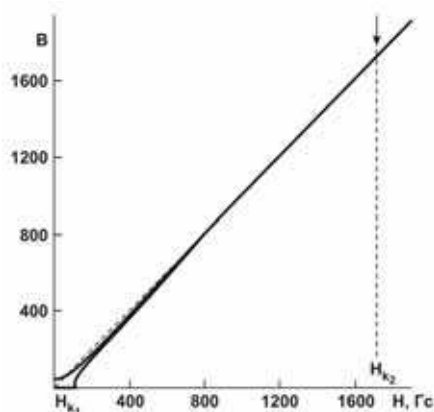

Fig. 13. B-H curve of long cylindrical sample of single crystal Pb+66,7at.%Tl in longitudinal field (Rjabinin & Shubnikow, 1935b).
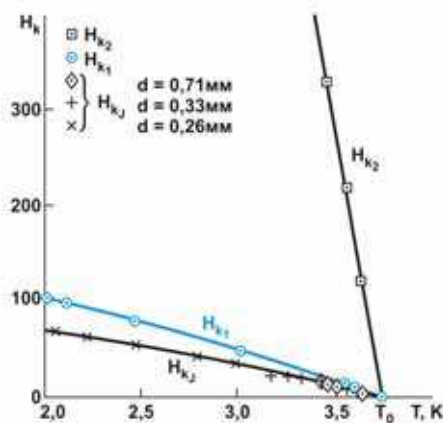

Fig. 14. Temperature dependents of H_{c1}, H_{c2}, H_{cj} for single crystal Pb+66,7at.% Tl (Rjabinin & Shubnikow, 1935a).

Note that in the same 1935 C.J.Gorter (Gorter, 1935) and H.London (London, 1935), while discussing the behavior of alloys with a large critical field in the absence of inhomogeneities, arrived at a conclusion that in magnetic field they had to be delaminated into thin (smaller than λ) superconducting laminae which ran parallel to the applied magnetic field and were separated by thin normal layers. An assessment of those efforts was quick to come in the first edition of the Shoenberg monograph (Shoenberg, 1938): "*De Haas and Casimir-Jonker (De Haas & Casimir-Jonker,1935b; De Haas & Casimir-Jonker,1935c), using the bismuth wire technique, showed that actually a magnetic field penetrated into an alloy long before it was large enough to restore the first trace of resistance, and that the penetration was very nearly complete at field strengths of the same order of magnitude as for pure elements. Similarly, Mendelssohn and Moore (Mendelssohn & Moore, 1935), and Rjabinin and Shubnikov (Rjabinin & Shubnikov, 1935a; Rjabinin & Shubnikov, 1935b), measuring the B-H curve of a long rod of superconducting alloy, found that B ceased to be zero, and approached the value of H, at fields much lower than those required to restore the first trace of resistance.*»

The Mendelssohn Sponge hypothesis was predominant for about 25 years used to explain the superconducting alloy properties. It would be just enough to mention a monograph "Superconductivity" by V.L.Ginzburg edited by L.D. Landau (Ginzburg, 1946) where it is said that "*The superconductor properties are strongly dependent on impurities, tensions and various inhomogeneities of their composition and structure. The properties of the alloys in which these inhomogeneities are actually always present are substantially different to those of the pure superconductors*". The Mendelssohn Sponge hypothesis was later found erroneous (refer, for instance, to (Goodman, 1964; Berlincourt, 1964; Morin et al., 1962; Berlincourt, 1987)).

We shall reiterate that nearly all of the alloy samples studied in all above works (except alloys Pb-Tl and Pb-Bi (1-10wt%)) had more than one phase, hence they were explicitly inhomogeneous.

Even though 9 out of 13 of the above-mentioned experimental studies on superconducting alloys pursued for 7 years by men of science from different countries W.J.De Haas, J.O. Wilhelm, K. Mendelsson, L.V. Shubnikov with co-workers (De Haas & Voogd, 1929; De Haas & Voogd, 1930; De Haas & Voogd, 1931b; De Haas & Casimir-Jonker, 1935a; De Haas & Casimir-Jonker, 1935b; De Haas & Casimir-Jonker, 1935c; Casimir-Jonker & De Haas, 1935; Tarr & Wilhelm, 1935; Keeley et al., 1934; Mendelsson & Moore, 1935; Mendelsson 1935; Yu.N. Ryabinin & Shubnikov, 1935a; Ryabinin & Shubnikov, 1935b) were published in high-rating journals ("Nature", "Commun. Phys. Lab. Univ. Leiden"), they were hardly referred to at a later time. Suffice it to say that the fundamental publication Handbuch der Physik of 1956 edition (Serin, 1956; Bardeen, 1956) did not mention any of the above-said research at all.

3. Discovery

Such was the status of research on magnetic properties of superconducting alloys around the globe by the time when the papers by L.V.Shubnikov, V.I.Khotkevich, G.D.Shepelev, Yu.N.Ryabinin (Schubnikow et al., 1936; Shubnikov et al., 1937) saw the light. Those papers submitted for publication on *April 11 and November 2, 1936,* respectively, contained the results of thorough studies across a broad temperature interval on magnetic properties of single-crystal metals and single crystals of single-phase alloys Pb-Tl (0.8; 2.5; 5; 15; 30; 50wt.%) and Pb-In (2; 8wt.%), which were very carefully annealed at the pre-melt temperatures.

Those are model alloys employed for research into Type II superconductors, since in a broad region of the impurity concentrations there is a region of the solid solution (Fig.7,15) which

was stable down to the cryogenic temperatures, thus opening up new vistas for making studies on the concentration effects.
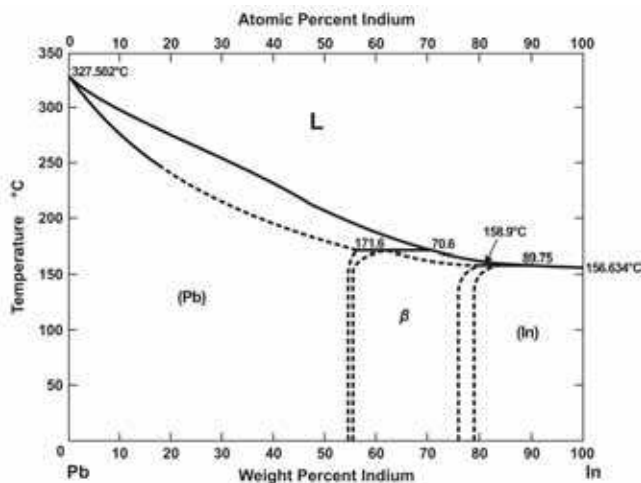

Fig. 15. Binary phase diagrams of the alloy Pb-In (After Massalski, 1987).

High-quality single-crystals of the alloys that had the length-to-diameter ratio ≥ 10 were grown according to the Obreimov-Shubnikov technique (Obreimow & Schubnikov, 1924). The magnetic moment of sample in a longitudinal homogeneous, constant pre-assigned magnetic field was measured over response of the ballistic galvanometer, while the sample was fast removed (or brought in) across the limits of a pickup coil connected to the galvanometer. The entire sample magnetization cycle went by the consecutive applied magnetic field variation.

In their articles (Schubnikov et al., 1936; Shubnikov et al., 1937) the authors implying the previous published papers (Rjabinin & Schubnikow, 1935a; Rjabinin & Schubnikow, 1935b) said again that "*In our first paper on the study of superconducting alloys we pointed out the possibility to explain the unusual magnetic properties of superconducting alloy by the disintegration of solid solutions at low temperatures*".

Besides, the authors indicated that: "*De Haas and Casimir-Jonker (De Haas & Casimir-Jonker, 1935b) found for the first time that, for $PbTl_2$ and Bi_5Tl_8, there exists the critical magnetic field which penetrates into the alloy but does not break up the superconductivity; that is why it is considerably lower than the critical magnetic field, at which the alloy acquires the ohmic resistance.*"

L.V.Shubnikov et al. (Schubnikow et al., 1936; Shubnikov et al., 1937) discovered that:

1. There was a boundary over the impurity concentration in the superconducting alloys before which their magnetic properties resembled the magnetic properties of pure superconductors – the total Meissner Effect at fields that were smaller than critical and a sudden disruption of the superconductivity upon further magnetic field increasing (Fig.16).

2. Upon increasing the impurity concentration beyond that boundary (within the present-day viewpoint: with the growth of the Ginzburg-Landau parameter æ) the magnetic properties of the alloys got to differ drastically from those of the pure superconductors: The Meissner Effect existed only as far as the magnetic field H_{c1}, and upon further field increasing the alloys remained superconducting as far as H_{c2}, with the magnetic field

gradually penetrating into the alloy. Fig.17,18 gives the results of research on alloys Pb-Tl, and Fig.19 does that for Pb-In.
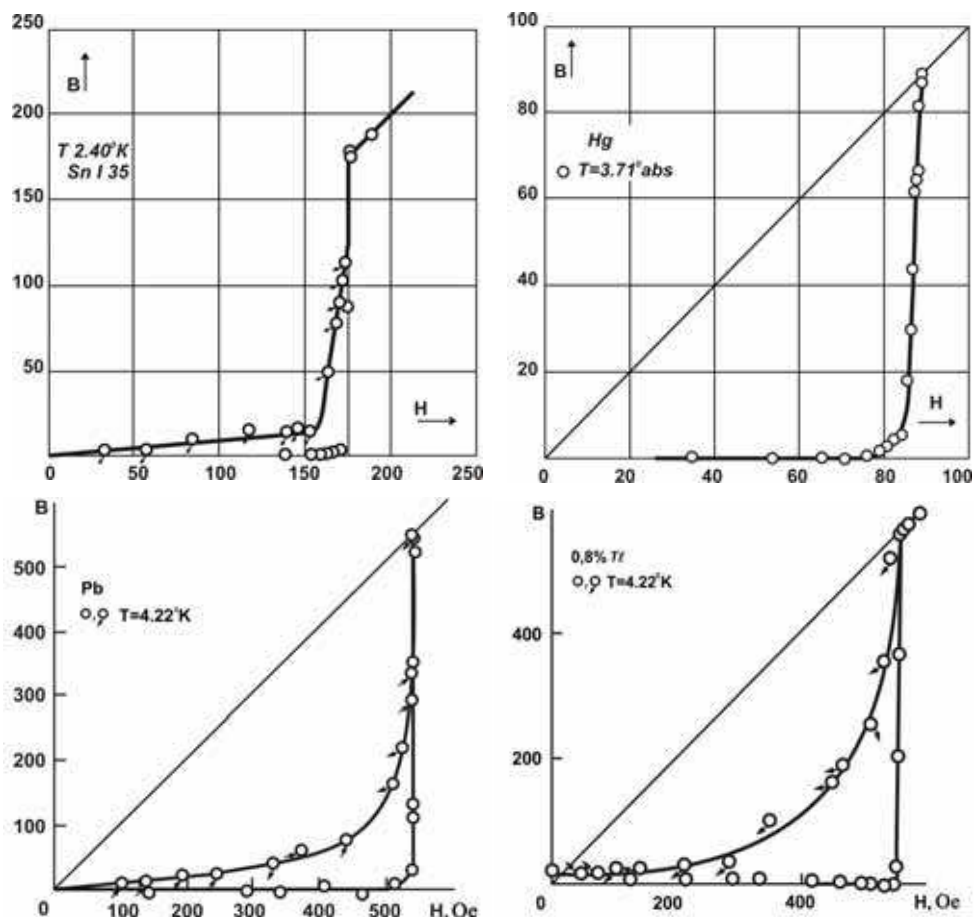

Fig. 16. The induction curve of long cylinders of pure single-crystal Sn, Hg, Pb and single-crystal alloy Pb+0,8wt%Tl in longitudinal magnetic field (After Schubnikow et al., 1936).

3. With increasing the impurity concentration (i.e. with a growing parameter æ) the interval between H_{c1} and H_{c2} broadened, i.e. H_{c1} got smaller, while H_{c2} grew. Fig. 20 presents data for alloys Pb-Tl.

4. The unusual properties found on the superconducting alloys could not be attributed to the hysteresis phenomena, since at high increasing and decreasing fields the phenomenon was well reversible, the hysteresis rather small.

5. The difference in free energy of magnetized and normal superconductors was given by the area of the curve:

$$\Delta F = \int M dH,$$

where M – the magnetization, while the entropy difference was produced by the derivative:
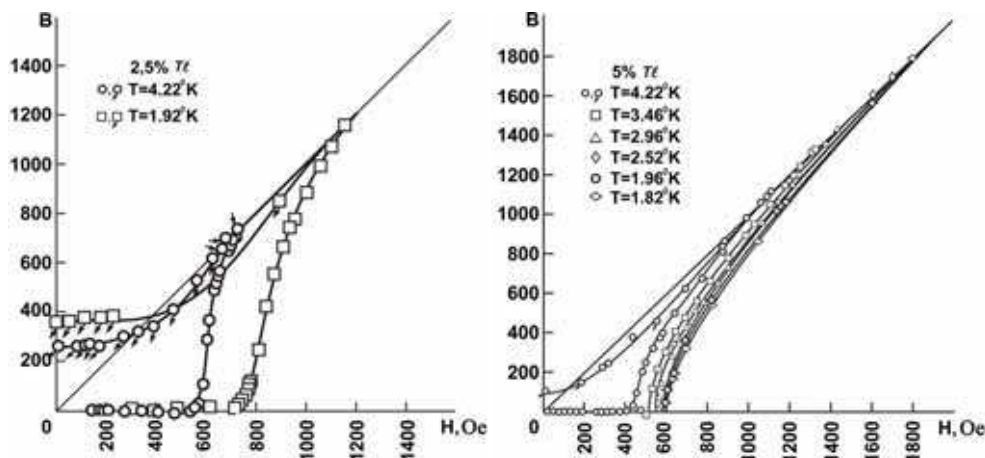
$$\Delta S = - (\partial F / \partial T)_B.$$

Fig. 17. The induction curve of long cylinders of single-crystals of alloys Pb+2,5wt%Tl; Pb+5wt%Tl (After Schubnikow et al., 1936).

The computation of the entropy difference made in reference (Schubnikow et al., 1936; Shubnikov et al., 1937) for these alloys indicated that in this case, as in the case of pure superconductors, the researchers dealt with magnitudes of the same order that were likewise dependent on temperature. For this reason, the jump in the heat capacity during the superconducting transition in zero magnetic field for the alloy was comparable to that of a pure superconductor.

6. The X-ray studies made on the superconducting alloys indicated that they had no solid solution disintegration going in them (the alloys were single-phase) which conflicted with the old ideas about their superconducting properties being related to the inhomogeneities.

In this way, it was exactly in the research papers by Shubnikov, Khotkevich, Shepelev, Ryabinin (Schubnikow et al., 1936; Shubnikov et al., 1937) that a well-substantiated and correct conclusion was made as to the existence of a new superconductor type. This conclusion clashed with all the preceding research that had explained the previously obtained results by compositional and structural inhomogeneities of samples.

Even though the published results by L.V.Shubnikov et al. (Schubnikow et al., 1936; Shubnikov et al., 1937) became instantly known abroad (Wilson, 1937; Ruhemann, 1937; Shoenberg, 1938; Jackson, 1940; Burton et al., 1940; Mendelssohn, 1946; Shoenberg, 1952), they were running long ahead of their time and their significance had not been appreciated for what they were for a very long time to come.

The reason for this was clearly stated in the Nobel Prize lecture by V.L.Ginzburg (Ginzburg, 2004) where he, while discussing his and Landau's phenomenological theory of superconductivity (Ginzburg & Landau, 1950), remarked that regarding the superconducting alloys: *"an understanding of the situation was lacking, and Landau and I, like many others, believed that alloys are an 'unsavory business', and did not take an interest in them, restricting ourselves to the materials with æ < æ$_c$, for which σ_{ns}>0, i.e. type I superconductors".*

Much later after the Ginzburg-Landau theory had been constructed (Ginzburg & Landau, 1950) an appreciation was given with reference to the studies made by Shubnikov and his co-workers (Schubnikow et al., 1936; Shubnikov et al., 1937) that *"The most spectacular application of the Ginzburg-Landau theory has been to a description of such superconductors"* (Chandrasekhar, 1969). Berlincourt (Berlincourt, 1987) noted very justifiably that Shubnikov et al. did not use in their research the C.J.Gorter (Gorter, 1935) and H.London's Theory (London, 1935). On the other hand, neither C.J.Gorter, nor H.London referred to Shubnikov's et al. results to support their theories. It would be very apt to cite the R.Kipling's "Oh, East is East, and West is West, and never the twain shall meet…".
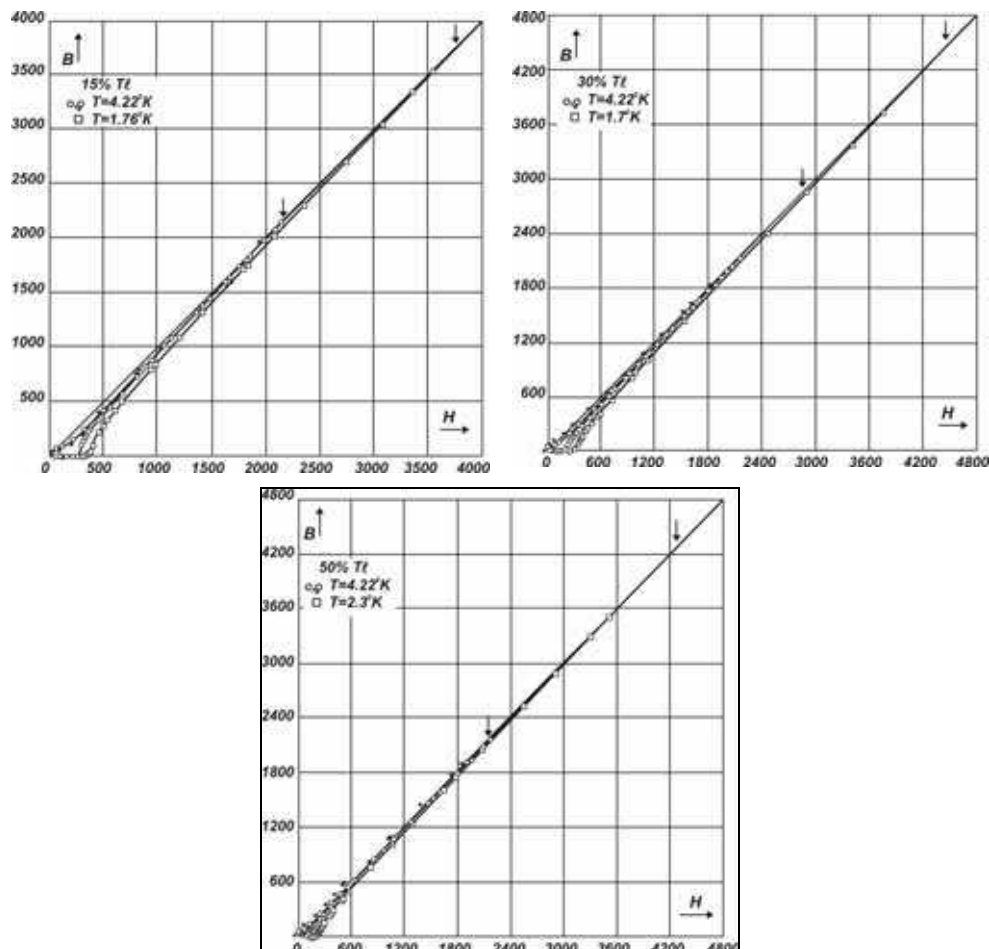

Fig. 18. The induction curve of long cylinders of single-crystals of alloys: Pb+15wt%Tl; Pb+30wt%Tl; Pb+50wt%Tl (After Schubnikow et al., 1936).

The discovery discussed above was accompanied by a dramatic conflict of creativity and a great human tragedy affecting the lives of two prominent scientists, L.D.Landau and

L.V.Shubnikov, and the directions the Big Physics might otherwise have taken. V.L.Ginzburg, a Nobel Laureate, addressing an International Conference of Fundamental Problems of High-Temperature Superconductivity (2004) had the following to say, "*Shubnikov and his students and colleagues accomplished a lot within only a few years, and I should specially mention his studies of superconducting alloys and a factual discovery of Type II superconductors. I am sure that Shubnikov would have achieved even greater success in science, and one cannot but feel bitterness about his untimely (at the age of only 36!), and quite guiltless death under the ax of Stalin's terror*" (Ginzburg, 2005).
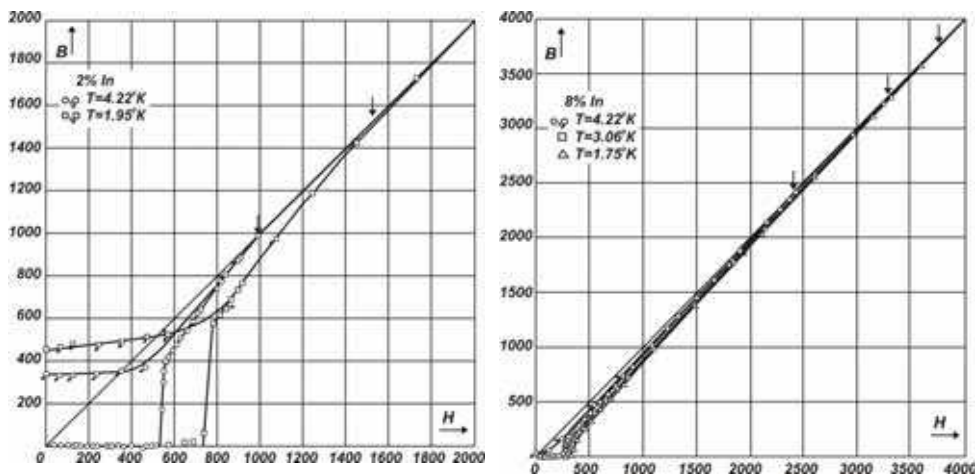

Fig. 19. The induction curve of long cylinders of single-crystals of alloy Pb+2wt%In; Pb+8wt%In (After Schubnikow et al., 1936).

The dramatic conflict of creativity concerned his close friend L.D. Landau with whom they had such lively discussions on all ongoing work at Shubnikov's Lab. L.D. Landau did not recognize the experimental discovery by L.V.Shubnikov and co-workers (Schubnikow et al., 1936; Shubnikov et al., 1937) either in 1936 (it is known as fact that the publishing of the articles (Schubnikow et al., 1936; Shubnikov et al., 1937) was delayed by more than 3 months, because Shubnikov failed to "run" them through Landau (Slezov et al., 2007)), or in 1950 when he and V.L.Ginsburg created the phenomenological theory of superconductivity (Ginzburg & Landau, 1950; Ginzburg, 1955) wherein the Ginzburg-Landau parameter æ was brought into the picture. In his paper published in 1997 and titled "Superconductivitry and superfluidity (what I could and could not do)", V.L.Ginzburg, discussing the theory (Ginzburg & Landau, 1950; Ginzburg, 1955) pointed out quite clearly, "*In this way, we actually overlooked the possibility of existence of Type II superconductors*" (Ginzburg, 1997).

The Great Human Tragedy was such that on August 6, 1937 L.V.Shubnikov was arrested without a warrant, and by the joint verdict of October 28, 1937, handed down by the odious functionaries of the Totalitarian Regime, Yezhov and Vyshinsky, he was shot dead (rehabilitated in 20 years) (Fig.21).

L.D.Landau was arrested on April 27, 1938, now as a staff scientist at Institute of Physical Problems, however in a year he was pulled out of jail by P.L.Kapitsa's intervention (L.D.Landau was also granted the pardon posthumously only in 1990). As a reminder, we

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