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OF VARIOUS LEAD-BASE ALLOYS

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ABSTRACT

The superconducting transition temperatures T_c of lead-base alloys with 1-7 at.% Cd, Hg, In, Tl, Sn, Sb, and Bi have been measured. T_c changes linearly with solute concentration. For the light solutes In, Sn, and Sb, T_c is higher than for the heavier elements of the same group of the periodic table. The reason for this seems to be a change in the phonon spectrum, caused by alloying.

Moreover T_c has been measured for the system Pb-In in the range 0-65 at.% In. T_c decreases monotonically with increasing In content, in contrast to earlier findings for the system Pb-Tl.

I. INTRODUCTION

The BCS theory allows one to express the superconducting transition temperature T_c as a function of three parameters: the density N(0) of electron states at the Fermi surface in the normal conducting phase, a parameter V, which describes the coupling between electrons and phonons, and ν_D, the Debye frequency

$$\frac{1}{N(0)V} = \int_0^{h\nu_D} \left(\tanh \frac{E}{2kT_c}\right) \frac{dE}{E} \tag{1}$$

k = Boltzmann's constant,

h = Planck's constant.

For weak coupling superconductors, for which the product N(0)V is small, this reduces to the well-known formula

$$kT_c = h\nu_D \exp\left(-\frac{1}{N(0)V}\right) \tag{2}$$

The Debye frequency enters these expressions because in the BCS theory the phonon spectrum is approximated by the Debye distribution, which is characterized by ν_D.

The dependence of T_c on ν_D, N(0), and V has been investigated by a great number of authors. The results are summarized in the following:

1. Debye frequency ν_D:

This problem is normally referred to as the isotope effect. As ν_D is proportional to $1/\sqrt{M}$, where M is the atomic mass of the material involved, T_c should also be proportional to $1/\sqrt{M}$. This has been experimentally proved for the different isotopes of various elements, but some

transition elements show a weaker dependence $T_c(M)$. An explanation for this has been given by J. W. Garland.[1]

2. Coupling parameter V:

D. Farrell et al.[2] have been able to explain the critical temperatures of various zinc-base alloys by calculating V as a function of alloy composition.

3. Density of electron states N(0):

The dependence T_c on N(0) has been investigated most extensively. N(0) can be varied by adding atoms of a different number of valence electrons to the base material,[3-8] thus changing the Fermi energy and by this N(0). In this connection M. F. Merriam's[7,8] measurements of T_c for different alloy systems are of special interest: he has been able to show that as soon as the Fermi surface interacts with Brillouin boundaries, a sharp change of T_c occurs, reflecting the strong change of N(0). A study of T_c versus composition has been done recently by T. Claeson[9] for the system lead-thallium. He found a depression in the plot T_c versus composition at 49.5 at.% Tl (Fig. 1). Using data published by J. R. Anderson and A. V. Gold[10] on the electron structure of pure lead and applying the rigid band model T. Claeson finds that this 49.5 at.% Tl-alloy should have a very high N(0) because the electron concentration of this alloy is very close to that for which electrons start entering the third band. But according to the BCS formula, Eq. (1), relating T_c to N(0), one expects a high and not a low T_c, though there could be a difference in electron-phonon coupling for electrons of different bands. T. Claeson was not able to rule out completely the possibility of some phase change, such as ordering.

Therefore in this investigation T_c has been measured over the whole solubility range for the system lead-indium, because indium belongs to the same group in the periodic chart as thallium.

As there is a rather great discrepancy between the published (H. Gamari-Seale and B. R. Coles[6] and M. Sato et al.[11]) critical temperatures for dilute lead-base alloys with Cd, Hg, In, Tl, Sn, Sb, and Bi as solutes, these measurements have been repeated too.

II. EXPERIMENTAL PROCEDURE

1. Specimen Preparation

The materials were provided by the following companies: American Smelting and Refining Company (In, Tl, Pb, Sb, Bi), Cominco American Inc. (Sn, Cd), Masero Laboratories (Hg). According to the manufacturers the impurity contents of the starting materials was less than 10 ppm. The weighed amounts of lead and solute were sealed in quartz tubes, i.d. 6 mm, under a helium atmosphere of 10 Torr. Thallium was never exposed to the open air, but only handled in a dry box under a helium atmosphere. There was no visible evidence of thallium oxidation. The solute concentration has been calculated from the weights of the constituents. The specimens with indium contents between 6 and 65 at.% were agitated for 24 hours at 380°C in a rocking furnace, quenched in ice water, and then annealed for 36 hrs at a temperature 20-30°C below the solidus line, which has been established by T. Heumann and B. Predel.[12] This annealing treatment proved to be sufficient for homogenizing the specimens. Specimens with solute concentrations below 6 at.% were mixed for 48 hrs at 440°C in the rocking furnace, quenched as above, and homogenized for at least 40 hrs at the following temperatures: In, Tl at 295°C; Cd, Sb at 250°C; Hg, Sn, Bi at 183°C. These temperatures had been chosen to make sure that the compositions of the alloys were within the solubility-limits. After the homogenization the specimens were again quenched in ice water and immediately transferred to liquid nitrogen temperature. As annealing the specimens for 10 min at 32°C did not change their T_c, it was certain that no precipitation had occurred during the quench from the annealing temperatures.

2. Cryogenic Equipment

The superconducting transition was detected by measuring the mutual inductance of two coaxial coils, containing the sample. A germanium resistor was used as a thermometer. It has been calibrated between 4.5 and 5°K against the vapor pressure of helium, at 7.193°K against T_c of pure lead. This value has been reported by J. P. Franck and D. L. Martin.[13] Between 5° and 7.193°K the thermometer has been checked against another germanium resistor, the calibration of which can be traced back to NBS. Absolute errors of measured T_c values are estimated to be less than 0.015°K, whereas relative errors are assumed to be less than 0.002°K.

To speed up measurements six coils, each for one specimen, were enclosed in a heavy copper-block, which also contained the germanium resistor. The coils had a primary and a secondary winding, the output of the latter was amplified, and together with the resistance of the thermometer recorded on a multi-channel recorder. The ac-magnetic field, produced by the primary, was about 10^{-3} G, and the frequency used about 130 Hz. The earth's magnetic field was not compensated, although it could produce a change in T_c of the order of magnitude of 10^{-3}°K. Therefore a pure lead specimen has always been measured together with the low-solute-concentration specimens, in order to be able to allow for changes in the external field. The scatter of T_c for the pure lead sample was less than 0.0015°K. Attached to the copper-block was a heater, and the whole assembly was enclosed in a gas-tight copper-box, which was filled with 760 Torr helium at room temperature. First this box was immersed in liquid helium to cool the specimens to a temperature well below T_c. Then the box was raised above the level of the liquid helium. A temperature sweep-rate

of about 0.003°K/min was established by heating the copper-block constantly, but varying the evaporation rate of the liquid helium by changing the power input in a resistor placed in the liquid helium.

T_c was defined as the temperature at which the signal coming from the secondary coil was the average of those for the completely normal and completely superconducting specimen. The hysteresis in T_c measured in warming up or cooling down was on an average 0.001°K. The half-width of the transition, defined as the temperature-difference between 25 and 75% of the whole signal change, was on an average 0.008°K. For solute concentrations below 10 at.% the temperature-difference for a signal-change from 5-95% was always less than 0.020°K.

III. RESULTS

1. Pb-In

About 50 samples, covering the whole solubility range from 0-65 at.% In, have been tested. The results are shown in Fig. 1, together with three points measured by W. Meissner et al.[14] T. Claeson's data on Pb-Tl are also given. The points for indium can well be represented by

$$T_c = \sum_{V=0}^{6} a_V c^V \quad (c = \text{at.\% In}), \qquad (3)$$

with

$a_0 = 7.1478$ °K

$a_1 = -1.6324 \cdot 10^{-2}$ °K

$a_2 = 1.8995 \cdot 10^{-4}$ °K

$a_3 = -7.2011 \cdot 10^{-6}$ °K

$a_4 = 1.4243 \cdot 10^{-7}$ °K

$a_5 = -1.6951 \cdot 10^{-9}$ °K

$a_6 = 7.5755 \cdot 10^{-12}$ °K

The average difference between T_c calculated from Eq. (3) and measured is 0.0013°K, and the maximum difference 0.009°K. The two differences between the indium and thallium alloys are:

a. Indium affects T_c much less than thallium does.

b. Though 20 specimens with compositions between 46 and 54 at.% In have been tested, no deviations from a continuous decrease of T_c with increasing In-content has been detected.

But some special features have been found for a specimen, containing 50.00 at.% In after annealing it for a prolonged time below room-temperature: 14 d at (-18±1)°C decreased T_c 0.127°K and 14d at (-9.2±1)°C 0.077°K. Both annealing treatments increased the transition width by a factor of three. Similar effects have been observed for specimens containing 41-58 at.% In.

2. Cd, Hg, In, Tl, Sn, Sb, Bi in Pb

The influence of 1-7 at.% of these solutes on T_c is shown in Fig. 2a and 2b. Letting T_{co} be the transition temperature of pure lead, then for each alloy system the T_c values can be fitted to:

$$T_c - T_{co} = \tau + \left(\frac{dT_c}{dC}\right) C \ , \qquad (4)$$

with C the solute concentration. Data for τ and dT_c/dC are given in Table I; also quoted are the values for dT_c/dC which have been measured by H. Gamari-Seale and B. R. Coles,[6] and those which have been derived from a plot published by M. Sato et al.[11] From this it seems that M. Sato et al.'s data are more reliable than those given by Gamari-Seale and B. R. Coles. The reason for this may be the following: these authors used only specimens with less than 3 at.% solute, so that they had to separate by calculation the sharp decrease in T_c which occurs below 1 at.% solute. According to D. Markowitz and L. P. Kadanoff[15] this drop is due to smoothing out the anistropy of the energy gap.

Table I.

Data for τ and dT_c/dC.

	τ (in 10^{-3}°K)	dT_c/dC (in 10^{-3}°K/at.%)		
		This investigation	Gamari-Seale	Sato
Cd	-34.2	- 11.8	0	
Hg	-31.4	- 7.7	0	
In	-27.1	- 16.9	-10	-16.9
Tl	-18.7	- 24.5	-12	-23.2
Sn	- 6.1	+ 15.2	+16	+14.3
Sb	- 8.1	+134.5	+140	+133.0
Bi	-21.5	+42.3	+53	+38.3

IV. DISCUSSION

The decrease in T_c of the specimen containing 50 at.% In after being annealed below 0°C can be understood in the following way: recently T. Heumann and B. Predel[12] reported thermodynamic data, from which they concluded that there should be a miscibility gap, centered at about 50 at.% In and below 30°C. From their hypothetic phase diagram one finds that the 50 at.% In-specimen at -18° or -9°C should split up into two phases, one having an In-content of roughly 30 at.% and the other of about 70 at.%. Our method used to measure T_c may only show one transition in spite of two phases with different critical temperatures being present, if the phase with the lower T_c is embedded in the one with the higher T_c. But in any case the higher T_c cannot be missed. Therefore one expects for the discussed phase-separation a critical temperature corresponding to 30 at.% In, which would be higher than that for 50 at.% In. This is in contrast to the experimental findings that the low temperature treatment decreased T_c. An explanation for this discrepancy may be found in the well-known effect that the superconducting properties of a finely dispersed phase may be changed by a surrounding other phase. This has been extensively investigated by R. Hilsch and coworkers[16,17] for thin films. Using T. Claeson's[9] arguments one expects for an alloy with an indium content of about 50 at.%, a high density of electron states. It is interesting that centered at this composition one finds the miscibility gap. But in contrast to the findings for thallium no abnormal critical temperatures were found, when the indium specimens were annealed above room temperature. Possibly the exceptional behavior of T. Claeson's[9] Pb-Tl samples containing about 50 at.% Tl is also due to a miscibility gap in this alloy system.

Looking at the values for dT_c/dC listed in Table I it is striking that, with the exception of Cd, dT_c/dC is always larger for the lighter solute than for the heavier one of the same group of the periodic table. Tin alloys have to be compared with pure lead. The effects of light solutes on T_c have been studied theoretically by J. Appel.[18] This author calculates T_c by taking into account the change in electron structure and phonon spectrum, caused by alloying. How the light solute indium affects the phonon spectrum of lead has been investigated by J. M. Rowell et al.[19] and by J. G. Adler et al.[20] by tunneling experiments. Their results are as follows: the phonon spectrum of pure lead consists of two peaks, one at a phonon energy of 4.5 meV and one at 8.5 meV. There are no phonons with energies above 10 meV. Adding some atomic percent indium does not shift these two peaks much; it only decreases their height. But a new peak in the spectrum appears at a phonon energy of about 9.5 meV. This causes the rise in T_c. A quantitative comparison between measured dT_c/dC-values and J. Appel's calculations is not possible because it is not known how the electron structure is affected by the alloying and the change in phonon spectrum is only known for indium. But according to J. M. Rowell et al.[19] one can expect a high frequency peak in the phonon spectrum if the atomic weight of the solute is less than about 75% of the atomic weight of the solvent. Because the Debye distribution has been used to represent the phonon spectrum in the BCS formula, Eq. (1), this formula cannot account for these high frequency peaks. It is not possible to treat this as some kind of isotope effect. But one can see from Eq. (1) qualitatively that light solutes will raise T_c, because they will increase the Debye frequency.

Unfortunately it is not possible to check whether adding Ga, Ge, and As to Pb increases dT_c/dC still more than adding In, Sn, and Sb respectively, because their solubility in lead is too small. But there is one other example from the literature available: G. Chanin et al.[21] measured T_c for different indium-base alloys, including gallium and thallium as solutes. Their results are shown in Fig. 3. The light solute gallium increases T_c, whereas thallium decreases T_c of indium.

From this point of view it might be advisable for making superconductors with high critical temperatures to use one constituent with a low atomic weight.

An explanation for the fact that Pb-Cd alloys have a lower dT_c/dC than Pb-Hg alloys, though Cd is lighter than Hg, may be that the effect of the change in the phonon spectrum of the Cd alloys is masked by the influence on the electron structure.

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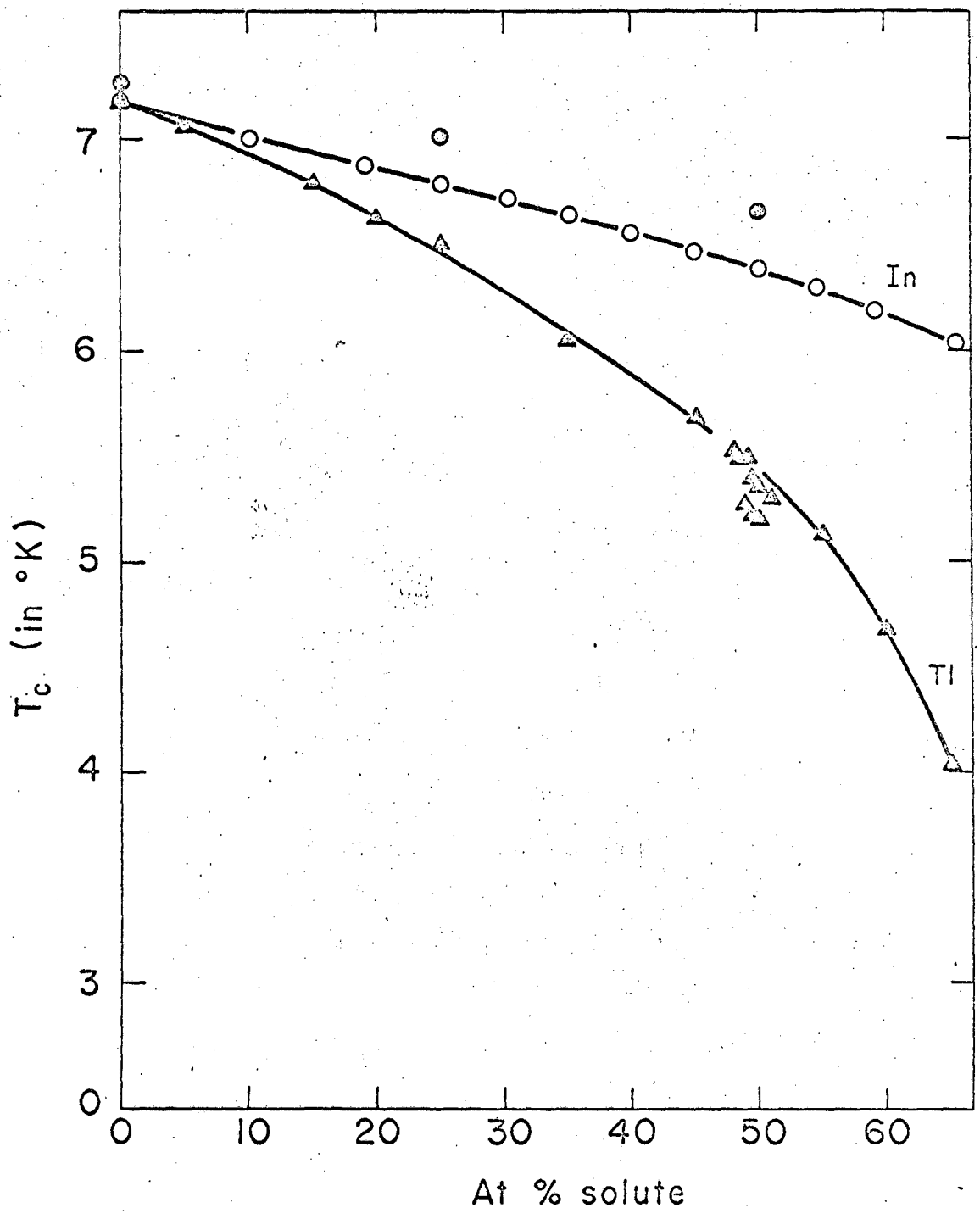

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Fig. 1 Critical temperature versus composition.
O In, this investigation; ⊙ In, W. Meissner et al.[14]
▲ Tl, T. Claeson[9]

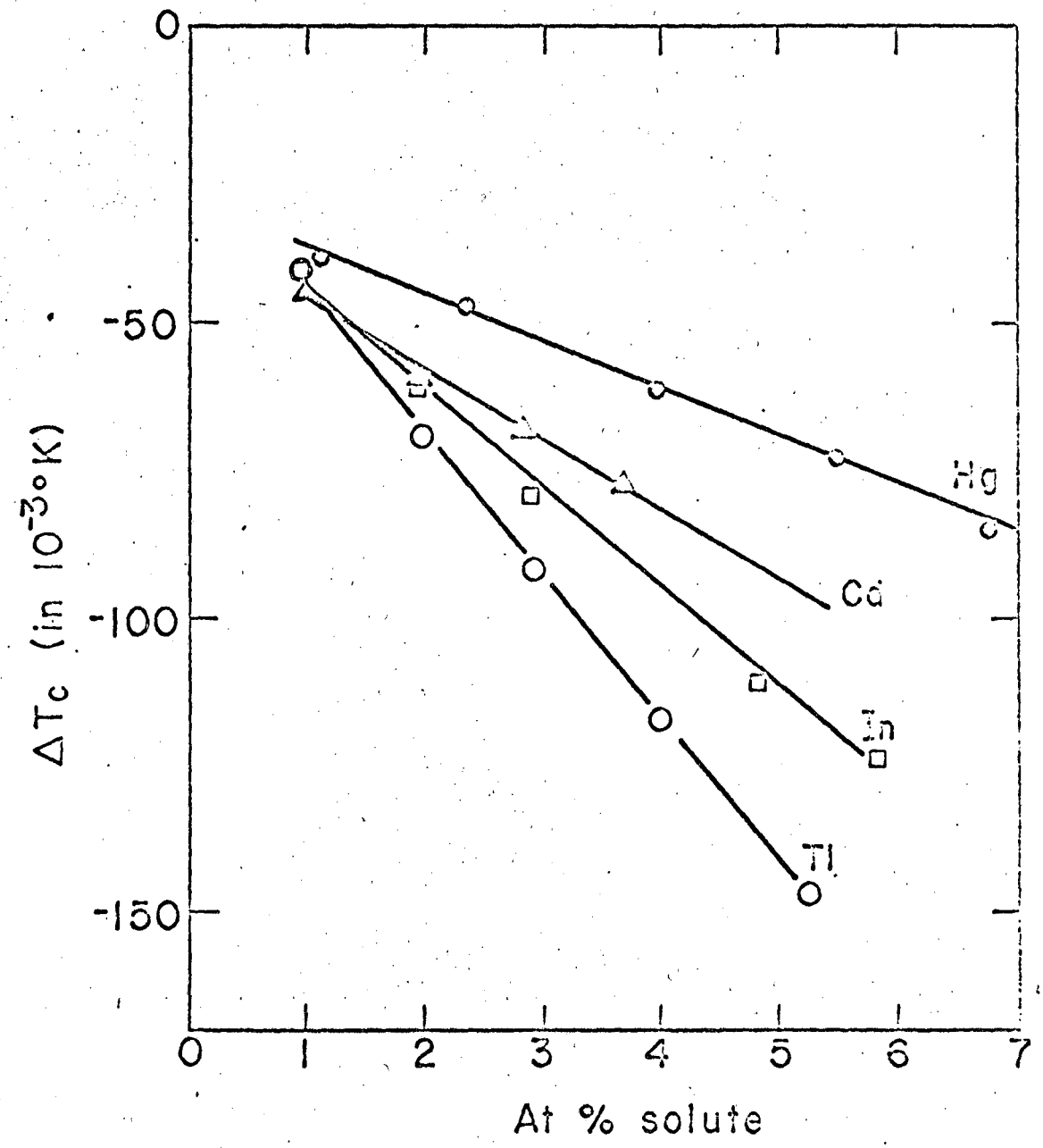

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Fig. 2a T_c for various dilute Pb-base alloys minus T_c for pure Pb.

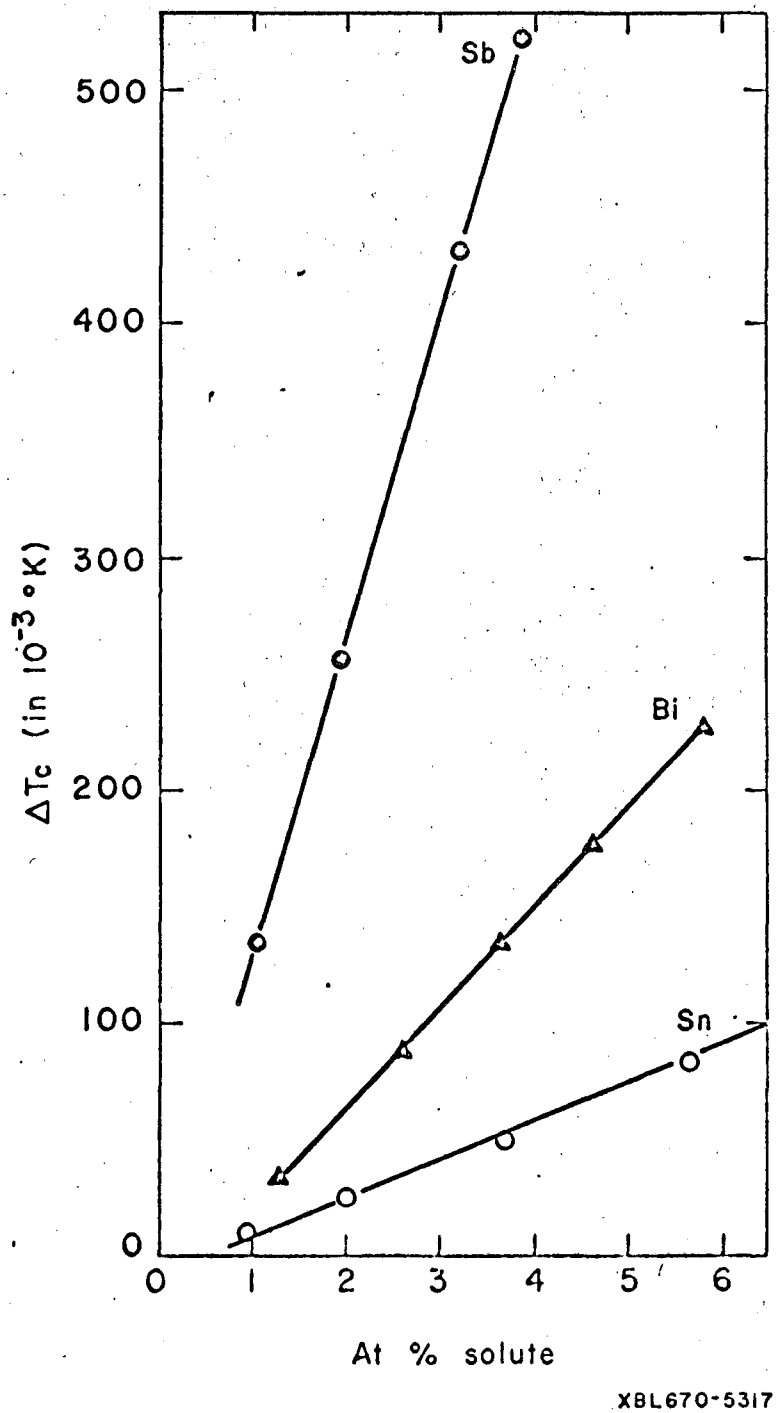

Fig. 2b T_c for various dilute Pb-base alloys minus T_c for pure Pb.

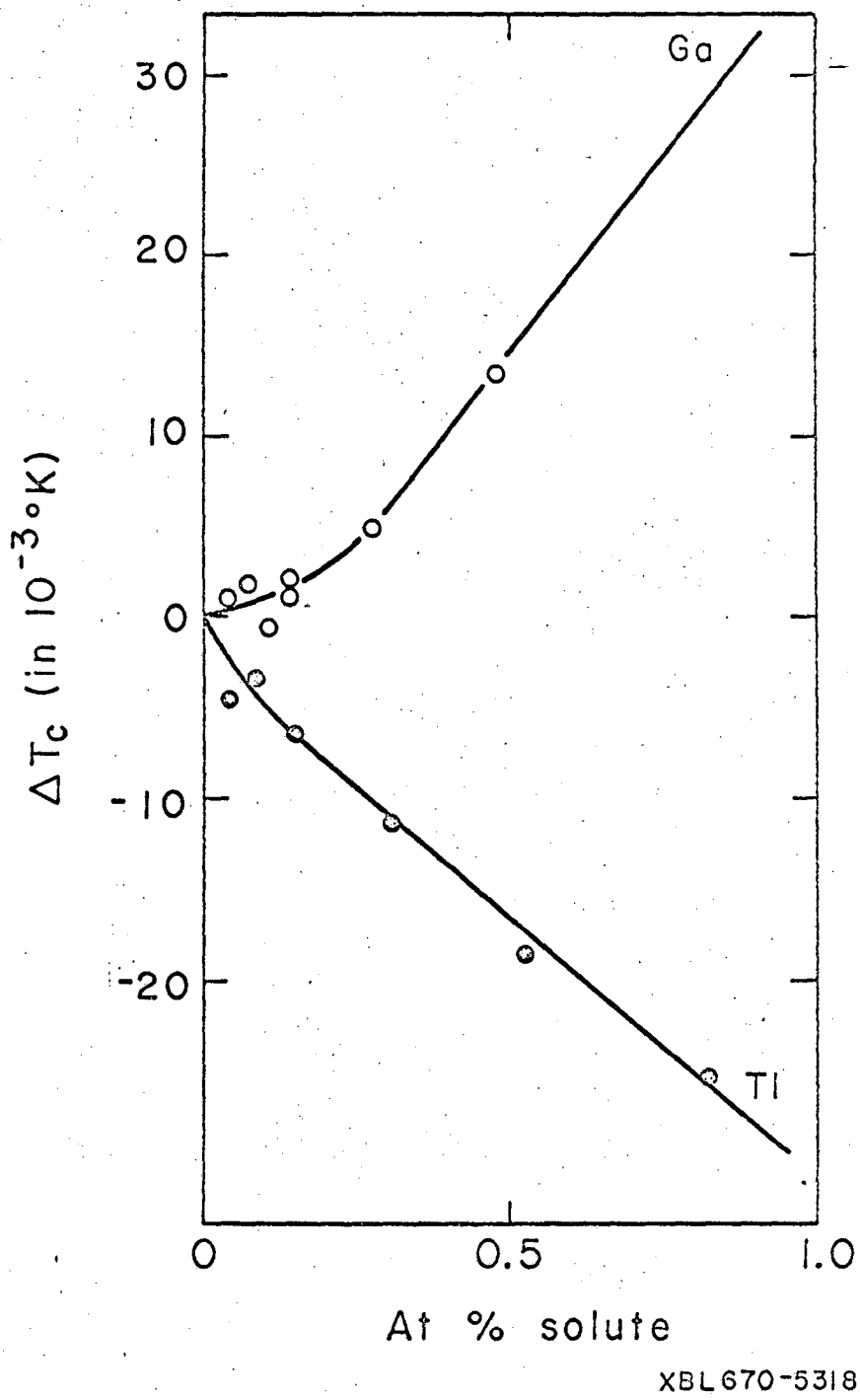

Fig. 3 T_c for In-base alloys minus T_c for pure In, after G. Chanin et al.[21]

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