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Empirical correlation between superconductivity and the Hall coefficient of metals

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Abstract. Superconductivity, resistivity and Hall Effect data for the noble metal alloys are compiled from the literature, measurements at room temperature for the Hall coefficient of Pb-Bi and Pb-Tl alloys are presented. The results support an extensive correlation between the superconducting transition temperature and the galvanomagnetic Hall coefficient of metals.

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1. Introduction

In this paper a report is given about some empirical correlations between the superconducting transition temperature, T_c, and the galvanomagnetic Hall coefficient $R(T)$ for a number of metallic conductors. Such a correlation was found a few years ago for a number of pure metals (Linde [1]), and was interpreted in terms of an assumed modified form of the paired charge carriers in the BCS theory of superconductivity (Linde [2]).

According to this correlation, low values of $|R|$ favour as a rule relatively high values of T_c for a given metal. It will be shown in the following that this correlation extends also to the data for several alloys. The values of T_c and R at room temperature, discussed below, have been mainly taken from the literature. In addition we report some results from new measurements on a number of Pb-based alloys (Pb-Tl and Pb-Bi).

2. Pure metals

The nature of the correlation between R and T_c can be illustrated from the electron band structure of simple metals. Figure 1 shows lines of constant energy in two dimensional k space which may be characteristic for a non-transition metal with only s and p electrons in the conduction band. The different curves (I–IV) in this figure may illustrate a section of the Fermi surface for different degrees of

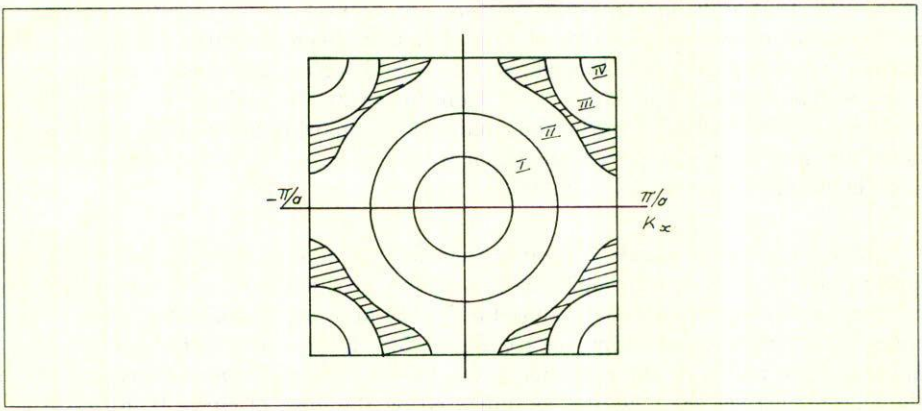

FIGURE 1. Hypothetical 2-dimensional constant energy contours.

filling of the bands. It is well-known that, on a surface such as I, for which the curvature is everywhere positive, the charge carriers are electron-like and give a negative contribution to R, while on surfaces such as IV with negative curvature, the charge carriers can be conceived as being hole-like and the corresponding contribution to R is positive. For fillings of the bands, characterized by Fermi surfaces such as II, both, electrons and holes, may be expected to contribute to the transport properties. Thus, for these metals there are both positive and negative contributions to R and a numerically small value of R may result.

In the modified Cooper-pair model mentioned above, the paired charge carriers are composed of one electron and one positive hole. On the bases of this model it was argued (Linde [1]) that the occurrence of both, electon-like and positive hole-like, carriers in the conduction band is a necessary condition for a given metal to become a superconductor. Equal or nearly equal concentrations of electron-like and hole-like carriers would result in low values of $|R|$ and would favour the occurrence of relatively high values of T_c. (Compare this to the transition temperatures in the order-disorder transition of alloys in the 50 at % region). We note that this pair model does not require that the Knight shift for the magnetic susceptivility of superconductors should decrease down to zero in the temperature region $T < T_c$. This is in contrast to the original Cooper-pair model but agrees with experimental results. A decrease is observed but doesn't get to zero even at $T = 0°\mathrm{K}$ (see also Linde [3]). Some further consequences of the modified pair model for the basic phenomena in the theory of superconductivity are treated in Linde and Rapp [4].

From data for the Hall coefficient (experimental and theoretical ones), it is in some cases possible to get information about the relative concentrations of electron-like and hole-like charge carriers in the conduction band. Only for monovalent metals it is, however, possible to obtain theoretical values by simple calculations. Agreement between the theoretical and experimental values implies,

as a rule, that only electron-like carriers are present in the conduction band of the metal concerned. Results of this kind have been obtained for the alkali-metals (see *e.g.* Kittel [5]). Accordingly the Fermi surface for these metals is free electron-like, such as I in figure 1, and only electrons contribute to the current and Hall conductivities. Clearly, the conditions for pairing between electrons and holes are absent in this situation which would correspond to the non-observed superconductivity in the alkali metals.

$|R|$ for the noble metals is smaller than for the alkalies corresponding to the larger electron density in the noble metals. In this case, however, calculations based on free electrons yield negative values for R with absolute magnitudes larger than those obtained experimentally (see *e.g.* Kittel [5]). In these nearly free electron-like metals, there may thus be portions of the bands with negative curvature where the charge carriers are hole-like, as indicated by the form of curve II in figure 1, and some electron-hole pairing could therefore occur.

The overall features of this correlation between R and T_c remain valid for all values of R as illustrated in figure 2 for the elements with only s and p electrons outside filled shells. The values of R, generally at room temperature, were taken from the Landolt-Börnstein tables [6]. Further details are given in Linde [1].

We now wish to extend this investigation by means of a study of R and T_c for several alloy systems.

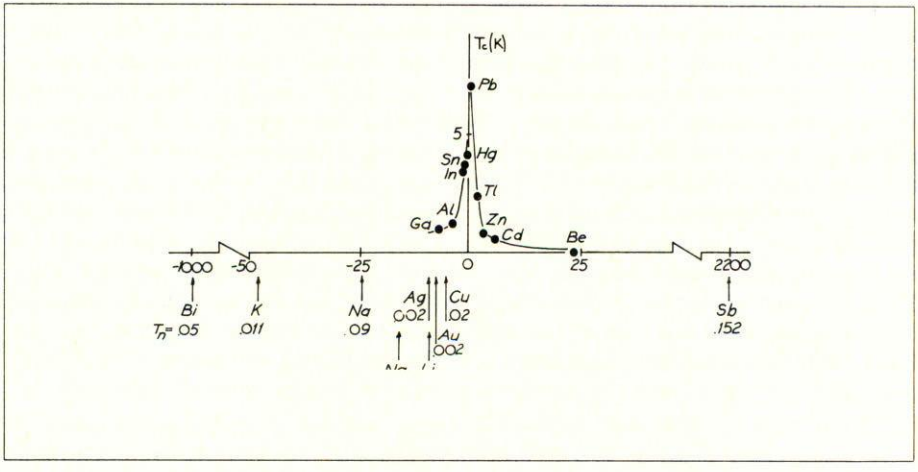

FIGURE 2. Correlation between R and T_c for metal elements with only s and p electrons. T_c denotes normal conductivity down to the temperature given. From Linde [1].

3. Noble metal alloys

An experimental approach to this problem consists of a study of noble metals under alloying. The addition of electrons to noble metal hosts will, on a rigid band model, increase the portions of the Fermi surface with negative curvature such as in the striated region of figure 1, resulting in an increased density of holes at the Fermi surface. An extension of the correlation between R and T_c would thus imply that an increased concentration of a polyvalent solute in noble metal hosts is accompanied by a numerical decrease of R and the occurrence of superconductivity. T_c would be expected to increase with solute concentration until the electron-like charge carriers come into a minority, and then a decrease of T_c is anticipated.

Comprehensive measurements of the Hall coefficient of noble metal alloys are available (Köster and Rave [7], Köster and Hank [8]). The overall behaviour of $|R|$ in these systems is a linear decrease with increasing solute concentration. In several alloy systems there is an initial increase in $|R|$ with a maximum at about or below 1 at % of solute, after which a more extended region of a linear decrease follows. This phenomenon has received particular attention. In the present context, it is a minor effect, however, since the description of the overall results is not affected by current interpretations of this maximum. Two separate contributions to R are distinguished (Hurd [9]): one arising from the band structure giving the linear decrease of $|R|$ and one from the anisotropy of the electron relaxation time giving the initial increase of $|R|$ which saturates at a fairly low solute concentration.

As mentioned above, the theoretical values of R for Cu, Ag and Au, calculated on basis of the free electron model, have higher negative values than the experimental ones. This difference is generally found to increase when the analysis is extended to noble metal alloys. We illustrate this by the data for AuZn alloys given in figure 3. Experimental data are from Köster and Hank [8], and the calculated values are based on the lattice parameter data of Owens and Roberts [10] and the assumption that each Zn atom contributes two electrons to the conduction band of the alloys. In terms of the model of electron-hole pairing, it is thus concluded that alloying of the noble metals would favour the occurrence of superconductivity.

Supporting these conclusions, superconductivity has been discovered in the fcc phase of 14 noble metal alloy systems (Hoyt and Mota [11], Mota and Hoyt [12]). Transitions were observable down to 7 mK in those investigations corresponding to a lower limit of solute concentration of about 3 at %. In all cases where results for a number of alloys in the same alloy system were reported, it was found that T_c increases with increasing solute concentration. T_c *vs.* R is plotted in figure 4 for the six Au-based alloy systems, where T_c has been measured. For the AuZn alloys the evaluation required extrapolation of the Hall effect data over a few at % of solute concentration. For comparison a few other alloy systems were similarly evaluated. In some cases, T_c was mesured for a few samples of one and the same composition. The separate values then obtained have all been plotted. The general

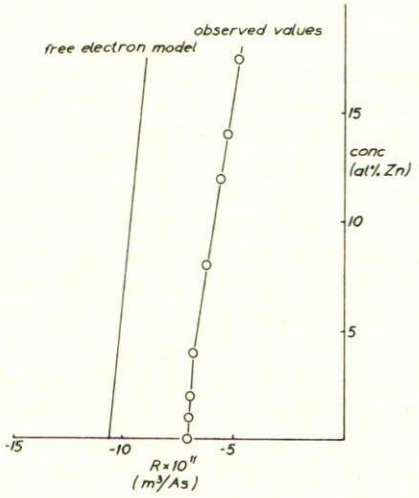

FIGURE 3. R *vs.* Zn concentration for AuZn. Points are from experiments by Köster and Hank [8]. The full line is the free electron value.

character of the correlation between R and T_c is the same as that in figure 2. This remains valid also when data from the literature for Ag and Cu-based alloys are included in a diagram like figure 4 although the values are then more scattered.

For noble metal alloys a general correlations between T_c (or the electron phonon interaction λ) and the temperature derivative of resistivity, $d\rho/dT$, above room temperature has been pointed out (Rapp [13]). Resistivity data are available for a large number of alloy systems (Linde [14]). From these data and the assumed correlation between λ and $d\rho/dT$, it is found that the correlation between R and T_c has an even wider range of applicability for noble metal alloy systems than that first observed. There are in all 27 alloys systems for which data on the concentration dependence of $d\rho/dT$ (Linde [14]) as well as R (Köster and Hank [8]) are available. In 25 of these systems the electron-phonon coupling, as inferred from the data of $d\rho/dT$, increases on alloying while $|R|$ decreases in agreement with the correlation between R and T_c. AuMg is particularly interesting because it is the only alloy system in these reports where $|R|$ increases with solute concentration. From resistivity data it is inferred that λ decreases with solute concentration in this system, but the correlation between R and T_c is again confirmed also in this anomalous case. Finally, for the remaining alloy system, CuMg, resistivity data indicate a decreasing λ while $|R|$ also decreases. It would thus seem that the correlation between R and T_c fails in this case. The effects are small however. Compared to the other anomalous system, AuMg, resistivity as well as Hall coefficient data for CuMg are restricted to smaller or much smaller

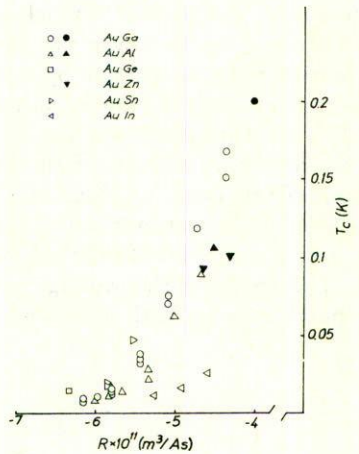

FIGURE 4. T_c *vs.* R for Au-based alloys. T_c data are from Hoyt and Mota [11] and Mota and Hoyt [12]. R data are from Köster and Hank [8]. Open symbols: Linearly interpolated Hall coefficients. Closed symbols: linearly extrapolated results. From Linde and Rapp [25].

concentration ranges. A more definite statement may therefore have to await additional measurements on CuMg alloys.

4. Pb-Tl and Pb-Bi

For further investigations regarding the validity of the correlation between R and T_c for alloy systems, two systems differing rather much from noble metal alloys were selected. The Pb-Tl and Pb-Bi systems are moreover interesting since they form continuous fcc solid solutions over wide ranges of concentration in which T_c varies over a range of values which is unusually large for non-transition metal alloy systems. The superconducting properties of these alloys have been investigated in detail (Dynes and Rowell [15]). Measurements of the Hall coefficient have also been reported (Takano and Sato [16]) which, for the Pb-Bi alloys, however, cover only a fairly limited concentration range. In order to follow the data of R further, we have extended these measurements farther into the Bi rich region. Additional results for new measurements on the Pb-Tl and dilute Pb-Bi systems are also reported.

Starting materials were metals of nominal purity 99.999 wt % or better (Materials Research Ltd). Appropriate quantities, thoroughly cleaned by etching, were melted and homogenized in an induction furnace at pressures below 10^{-6} torr. Weight losses were negligible. The samples were cold-rolled into foils and cut into

suitable form. The thickness was determined from the surface area, mass and, the density obtained from published X-ray data (Tyzack and Raynor [17] and Tang and Pauling [18]). Good thermal contact over the sample area was assured by using two Cu plates separated from the sample by mica and silicon grease. The Hall coefficient was measured with a dc current of only 200 mA in order to further reduce heating effects. The magnetic field was about 1 T and perpendicular to the surface of the foil. By repeated reversals of the magnetic field and current directions, various spurious effects could be eliminated, such as the voltage drop between the Hall proves due to the transport current and a small misalignment of the Hall probes, the Nernst and Righi-Leduc effects and thermal emf : s in the Hall voltage circuit. The resulting Hall voltage of the order of 100 nV was measured by a Tinsley potentiometer with a voltage sensitivity of about 10^{-9} volt.

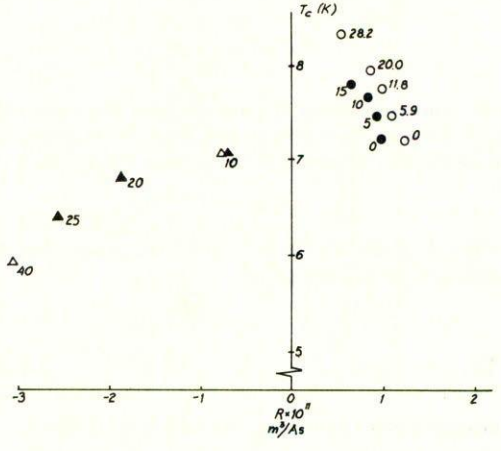

FIGURE 5. T_c *vs.* R for Pb-Tl (triangles) and Pb-Bi (circles). Open symbols present measurements, closed symbols: excepts of data from Takano and Sato [16]. Figures denote at % of solute concentration in Pb. T_c data were interpolated from Dynes and Rowell [15].

The results are shown in figure 5 where T_c is again plotted versus R (293°K) and the solute concentation in at % is marked in the figure. Values for T_c are from Dynes and Rowell [15]. The values of R for Pb and dilute PbBi alloys are somewhat higher than those reported in the literature (Takano and Sato [16]). The reason for this discrepancy of up to 20% is not clear. One possibility might be the different states of cold work and defect levels to which the Hall coefficient of Pb is apparently very sensitive (Bergman [19]). It is seen that the trend from the low concentration alloys is continued for the more concentrated alloys and extends all the way to just below about 30 at % Bi. For the PbTl system there is sign

reversal for R for low Tl concentrations after which $|R|$ increases with increasing concentration.

Divergent results have been reported for the maximum solubility of Bi in Pb Hansen [20] gives 23 at % while Elliot [21], quoting different investigators, puts the phase boundary at 19 and 32.5 at % respectively. From results of tunnelling measurements, Dynes and Rowell [15] conclude that the superconducting properties are very similar in the fcc and the neighbouring ϵ phase in this system. We attempted to prepare one more alloy with 35 at % Bi which is below the ϵ phase boundary. The Hall coefficient for this alloy was however large and negative (-7.8×10^{11} m^3/As) and was omitted from figure 5. This result may be due to a precipitation of a Bi rich phase during the rather slow cooling in the induction furnace.

The overall feature of figure 5, however, is a general confirmation of the correlation between R and T_c. Over a range of Pb-based alloys with solute concentrations extending to about 40 at % Tl and 30 at % Bi, a decrease of $|R|$ irrespective of the sign of R is accompained by an increase in T_c.

5. Concluding remarks

In conclusion we shall discuss some obvious limitations of the validity of the R-T_c correlation discussed in this report.

No universal curve between R and T_c has been obtained. It may be observed that the correlation between R and T_c for superconductors among the transition elements (Linde [1]) is of a similar nature to that shown in figure 2, but with the maximum values of T_c displaced in the direction of the positive R axis which may have its origin in the incompletely filled d-shells of these metals affecting the value of R but not that of T_c.

For alloys, the effective masses of holes and electrons in different portions of the bands can develop differently with the addition or depletion of electrons. Various such details of the electronic bands characteristic for different hosts will determine the delicate balance between negative and positive contributions to R and it is quite reasonable to expect R to change differently for a particular solute in different solvents or for different solutes in a given solvent. The discussion in connection with figure 4 illustrates this argument. The data for each alloy system are less scattered than all the gold based alloy data which are in turn less scattered than all the noble metal based data. Similarly, deviations from the correlation between R and T_c are not surprising in an alloy system when one component is varied over too wide a concentration range such as in the Pb-Tl system above about 40% Tl.

Another point worth mentioning is the different influence of disorder on R and T_c of Pb. With quench condensing at a low temperature, R of Pb will approach the free electron value (Koepke [22]), as expected for the liquid-like structure of amorphous metals while the T_c : s of Pb and PbBi alloys are only slightly affected by quench condensing (Petersen [23]). Apparently the correlation between R and T_c breaks down in such a case involving very large disturbances of the electron bands.

Finally, owing to the restricted availability of experimental data in the literature, only room temperature values of R have been used implying a complete neglect of the temperature dependence. In cases where this approximation is not justified, the effect is however often small for the scale of figure 2. There are cases where the temperature effect is however large. The interpretation of the R-T_c correlation of figure 2 may be affected in such cases as Zn and Cd where, in single crystals at low temperatures, there is a change of sign of R (Alderson *et al.* [24]).

In spite of these shortcomings due to an oversimplified model, we find the experimental evidence for a correlation between R and T_c quite impressive. It extends through the simple elements and (in a somewhat modified form) to some d band elements and a large number of alloys. Such a correlation has, to our knowlegde, not hitherto been deduced from observed data and its connection with basic theory of superconductivity certainly merits further investigation.

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Resumen. Se compila de la literatura los datos de superconductividad, resistividad y efecto Hall para aleaciones y metales nobles. Se presentan medidas a temperatura ambiente del coeficiente de Hall de los sistemas de aleaciones Pb-Bi y Pb-Tl. Los resultados apoyan una correlación muy extensa entre las temperaturas de transición a superconductividad y el efecto Hall de los metales.