The development of knowledge and understanding of the anomalous resistivity of diluted metallic solutions of transition metals

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factor to make the coincidence with the calculated curves as good as possible. We do therefore not consider our results as a quantitative check of Enderby and Walsh's results. However, they are a convincing evidence that the free carrier concentrations must be of the order 10^{22} cm^{-3} and the relaxation times 10^{-1} (eV)$^{-1}$ because it can be shown that a change of the order of magnitude of these quantities makes any reasonable agreement with the measured spectra impossible.

The measurements of magnetic susceptibility of molten CdSb by MATYÁŠ [8] are consistent with the picture obtained from the transport and optical data.

CdTe

The situation with CdTe is different. The emission spectra (Fig. 4) show that this material remains semiconducting even in the molten state. This is consistent with the conclusion obtained from the study of the electric conductivity [9, 10] that the covalent bonds are for a large part conserved through the melting point. The increase of carrier concentration during melting which causes an increase of electric conductivity is seen also in the optical data: before melting, R_q in the low energy range is constant, after melting it decreases down to a certain minimum. This is what one would expect on the basis of the picture suggested in References [9, 10].

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The Development of Knowledge and Understanding of the Anomalous Resistivity of Diluted Metallic Solutions of Transition Metals

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(14. V. 68)

In 1930 [1] MEISSNER and VOIGT (Berlin) published a long series of data on electrical resistance of several metals as a function of temperature. In the region of liquid helium the resistance at the lowest of 2 or 3 temperatures was higher by 0.5–2% for the metals Mg, Mo, Fe, Co and Pd, while its value indicated that the purity was poor. The authors paid little attention to the phenomenon, merely making the remark that it might be caused by the impurities and thus might disappear for purer materials.

In subsequent investigations carried out in Leiden [2] on the 'ideal' resistivity of metals, a minimum was found in the Resistance-Temperature curve (R-T) of the purest gold wires obtained from 'Heraeus' having a residual resistance ratio of 27×10^{-4}. In several wires of different origin the minimum in the R-T curve displaced to higher temperatures with increasing residual resistance, consequently with impurity [3b]. The wires with the highest residual resistance had been drawn through steel dies, which indicated that probably iron was the dominating impurity. Upon introduction of some iron during the treatment of silver wires a minimum appeared also in this metal. Among other influences that of gas was tested during the measurements at different temperatures. Unfortunately the influence of oxygen during the annealing at 500 °C was not yet investigated, otherwise it might have been possible that the anomalous behaviour had disappeared by means of the oxidation of the impurity Fe, just as more than 20 years later would occur.

The results of the several measurements of the resistance ratio could be represented by $r = f(T) + \boldsymbol{a}\, g(T)$ with an accuracy of a few percents, where $f(T)$ would be the 'Bloch' dependence on temperature, $g(T)$ a steadily increasing function at lower temperatures and '$\boldsymbol{a}$' dependent on concentration. This was going to be repeated and extended in 1955 in Ottawa by Pearson c.s. for Cu-Fe.

During world war II the phenomenon was discussed in the thesis of VAN DER LEEDEN (1940). The R-T curve was represented by $r(T) = r_{id}(T) + z_{ph} + z_{ch}\,(1 + c\,T^{-1/2})$, where z_{ph} and z_{ch} are the residual resistance ratios due to physical and chemical impurities resp. while $r_{id}(T)$ is the resistance ratio for an ideal lattice ('Bloch') [3b].

After the war research was started in several centra, the measurements of the resistance carried out by means of the potentiometric as well as the inductive method, the metals being Au, Cu, Ag, Mg, Al and Zn. CROFT et al. (Oxford), DUGDALE and MACDONALD (Ottawa) described the behaviour of gold wires at very low temperatures with a formula of the form $r(T) = \text{constant} - a \log T$ [3b]. ALEKSEEVSKII and GAIDUKOV (Moscow) [3b] proposed the relation $r(T) = A\,(\log T/T_{min})(1 + B\,\log T/T_{min})^{-1}$. Because of the $\log T$ term may be referred here to Kondo's paper of 1964.

Linde stated anomalies in the conduction properties of Ag-Mn at and below room temperature. A cooperative effort of the laboratories in Stockholm and Leiden (Gerritsen) resulted in the discovery of a minimum in the R-T curve for dilute alloys of Ag-Mn followed by a maximum for higher concentrations at lower temperatures. The mentioned couple investigated [4] diluted metallic solutions of transition metals of the first long period in Cu, Ag or Au. In Ottawa MACDONALD et al. [3b] observed the anomalies also for diluted alloys of In, Pb, Ga, Ge, Sn. Consequently they discussed whether the minimum in the R-T curve might be normal and discovered by better measuring techniques and materials. However, their experiments on the thermoelectric power of Cu with small amounts of impurities cancelled the above mentioned idea. Careful investigations of KNOOK et al. [3b,c] showed that in Cu-Sn-Fe alloys only the transition metal caused an anomaly and moreover that not every transition metal dissolved in noble metals causes a minimum in the R-T curve. A large number of unpaired spins in the d-shell (Cr, Mn, Mo, Fe, Os, Re) was an essential condition.

FRIEDEL and coworkers [3b] gave, starting from the virtual bound state concept, a rule of thumb for the occurrence of an anomaly at low temperatures: $p \cdot \Delta E \geqslant E_F/3$ where p is the number of unpaired spins, ΔE the energy difference between 2 parallel or anti-parallel spins in the impurity ion (~ 0.8 eV) and E_F the Fermi-energy. This rule could be verified by measurements of the electrical resistivity and of the specific heat [3b, c].

In the period 1953–1963 many different models and concepts were proposed for the explanation of the anomalous effects. After the resonance hypothesis by KORRINGA and GERRITSEN [5], reconsidered by Domenicali, two groups of models appeared: one starting from a molecular field concept, another from the exchange interaction between pairs of ions [3b]. By each group part of the anomalous properties could be explained, but never all of them.

In 1964, however, KONDO [6] published a calculation which accounted for the resistance minimum and its temperature dependence reasonably well. Starting from the assumption of the existence of non-interacting moments in a non-magnetic host metal KONDO calculated in second Born approximation the scattering of the conduction electrons. Attempting to evaluate the contribution to the electrical resistivity of diluted alloys he remarked that the exchange scattering cross section should diverge at low temperatures, causing the resistivity to increase logarithmically as the temperature approaches absolute zero. Kondo took Bloch's law for granted in his description of the R-T curve, this resulted in $T_{min} = 120\ C^{0.20}$ K for Cu-Fe (KNOOK's exp.: $T_{min} = 115\ C^{0.19}$ K). The R-T curve for Au-Fe, as measured by MACDONALD et al., could also be rather well represented by KONDO's formula over a wide temperature range. However, theoretical techniques based on many body perturbation theory, double time Green's functions or dispersion theory were applied to KONDO's Hamiltonian and a new electron state below a concentration independent temperature $T_K \simeq T_F \exp(-1/|J|\ N(0))$ emerged without logarithmic divergence. (T_K is the Kondo or Suhl-Abrikosov temperature.) In this formula T_F is the Fermi temperature of 10^4–10^5 K, $J = s - d$ exchange interaction constant, $N(0)$ = density of states of one spin orientation per atom in the host metal at the Fermi surface.

Several theoreticians (see [7]) suggested that at sufficiently low temperatures the spin of the localized moment will be totally compensated by the spin of a cloud of polarized conduction electrons. This state is analogous in some way to the Cooper pair in superconductivity. The suggestion of a 'phase transition' to such a zero spin state as the 'zero temperature result' of the Kondo scattering leads to the interesting conjecture that perhaps some of the impurities which at conventional temperatures are observed to have zero magnetic moment are actually the end product of a very high temperature condensation, localized in real space about the impurity, due to the Kondo scattering. The 'quasi bound state' below T_K is not strictly a low-temperature phenomenon. As mentioned above T_K depends exponentially on the exchange constant J between the localized d-electron spin and that of the conduction electrons and it can vary from millidegrees to thousands of degrees for small changes in J (SCHRIEFFER 1967 [7]).

Experimental evidence for the increasing spin compensation below T_K at lowering temperatures was found by several authors [8–14].

The limitation of the number of transition metals to those with a high number of unpaired spins in the d-shell (KNOOK et al.) for the cause of anomalies in the R-T curve at low temperatures, is now transformed in a dependence on the value of the Kondo temperature. For transition metals of the first long period in Cu and Au T_K is the lowest for Mn [7, 13]. The absence of a minimum in the R-T curve of Au-Co and Cu-Co at low temperatures [15] is due to a T_K of the order of 500 and 1000 K respectively, while for Ti and Ni in Au and Cu this temperature is an order of magnitude higher. For Au-V, the alloy for which LINDE [3b, c] found a minimum in the R-T curve above room temperature (1958), the value of T_K is about 300 K (KUME [13]).

By changing the value of $|J| \cdot N(0)$ introducing another metal in the base metal (ternary alloys) it seems possible to influence the value of T_K and in this way the occurrence of anomalies at low temperatures (SERACHIK c.s. [3c], HEDGCOCK c.s. [3c], CAPLIN c.s. [16], BÉTHOUX c.s. [17]).

STAR [18] considered the shift of T_K in more detail and also its influence on the magnetic ordering (maximum in the R-T curve) in Cu-Au-Fe alloys.

So recent advance in the interpretation of anomalous low-temperature phenomena, of which only that of the electrical resistivity was discussed above, has widened this field to much higher temperatures. A time interval of about 40 years was required to reach some fundamental understanding of the anomalies mentioned in this note. During this time many other solid-state problems were investigated and interpreted in the ETH Zürich under the leadership of Professor G. BUSCH to whom this short paper is dedicated.

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