Resistivity Anomaly near a Critical Point in Semiconductor Alloys

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A simple theory of the anomalous resistivity of alloy systems is presented with explicit evaluations of the temperature dependence of electrical resistivity in the vicinity of critical points. It is shown that in the neighbourhood of transition points the resistivity-temperature curve has a maximum, and that in the case of the second order transition the maximum is much more conspicuous than the one in the case of the first order transition. It is also shown that the smaller is $k_F$, the steeper the maximum, $k_F$ being the Fermi wave number.

§ 1. Introduction

Recently the semiconductor alloy in the $(\text{In}_3\text{As}_3)_{a}(\text{In}_2\text{Te}_3)_{1-a}$ section of the In-As-Te ternary system has been found to have a critical point at the fraction $x_c=0.9$ and temperature $T_c=820\degree C$. The mobility change near the critical point is observed by Gasson et al. and is studied theoretically by Parrott. In his studies, however, only the value of overall changes in the mobility is given near the critical point.

In the present paper we consider the resistivity due to fluctuating parts of an atomic fraction or of an order parameter, and examine the temperature dependence of the resistivity in some detail. In the vicinity of the critical point, the temperature dependence of the resistivity is calculated explicitly in the form of $|T/T_c-1|$ expansion. And it is shown that the resistivity-temperature curve has a marked maximum at $T_c$ when $k_Fd<1$, $k_F$ being the radius of the Fermi sphere and $d$ the interatomic spacing, and that the maximum becomes steeper as $k_Fd$ decreases. The temperature dependence of the resistivity near the critical point is shown to be similar to that of ferromagnetic metals in the $s$-$d$ exchange model and of the order-disorder effects in alloys which show the second order transition. In this connection we also examine the order-disorder phenomena in alloys with the first order transition. In this case also there appears a maximum in the resistivity-temperature curve, though the maximum is less pronounced than in the case of the second order transition.
§ 2. Calculations

Let \( x(r) \) be the local value of the atomic fraction at position \( r \) and \( \bar{x} \) the average value. Then after Parrott\(^2\) the perturbing Hamiltonian to conduction electron is of the form

\[
H' = E(x - \bar{x}).
\]

(1)

\( E \) will be nearly equal to the difference between energy gaps of two constituents of the alloy.\(^3\) The relevant matrix element to the scattering process \( k \rightarrow k' \) for a conduction electron is given by

\[
(k'|H'|k) = E x_{k'-k},
\]

(2)

where \( x_q \) is the Fourier component of the fluctuation of atomic fraction:

\[
x(r) - \bar{x} = \sum_q x_q \exp(iq \cdot r).
\]

(3)

Then the standard perturbational treatment\(^4\) gives the transition probability \( Q_{k'k} \) for the scattering process,

\[
Q_{k'k} = (2\pi/\hbar) E|x_{k'-k}|^2 \delta(\varepsilon_{k'} - \varepsilon_k).
\]

(4)

Here \( \varepsilon_k \) is the energy of a conduction electron in state \( k \) and a simple effective mass approximation is used in what follows: \( \varepsilon_k = \hbar^2 k^2/2m^* \). In thermal equilibrium at temperature \( T \) we replace \( |x_q|^2 \) by its mean value\(^5\)

\[
|x_q|^2 = k_B T/V(a + b q^2),
\]

(5)

where \( a \) stands for \( \partial f/\partial x^2 \), \( f \) being the density of free energy and \( b \) is nearly equal to \( k_B T/s/d \), \( d \) being the interatomic spacing.

In the semiconductor alloys in which the concentration of conduction electrons is sufficiently high, one must use the degenerate approximation. Thence solving the Bloch equation\(^5\) one obtains for resistivity \( \rho \)

\[
\rho/\rho_e = (T/T_e) \{1 - (a/4b k_F^2) \log[1 + (4b k_F^2/a)]\}.
\]

(6)

Here \( \rho_e \) is the value of \( \rho \) at \( T_e \) and is given by

\[
\rho_e = (m^* k_B T_e E^2 k_F) / (4\pi \hbar N e^2 \varepsilon_F b),
\]

(7)

where \( \varepsilon_F \) is the Fermi energy and \( \varepsilon_F = \hbar^2 k_F^2/2m^* \).

First of all we consider the case of the second order phase transition:

(a) The case of a solid solution such as In–As–Te ternary system or of order-disorder effects in AB alloy.

In order-disorder phenomena we regard \( x \) as the long range order parameter\(^9\) \( s \) through \( s = 2x - 1 \). Then we have\(^3,6\)

\[
a = \frac{8k_BT_e}{d^2} \times \left\{ \begin{array}{ll} (t - 1), & T > T_e \\ 2(1-t) \left[1 + \frac{9}{2} (1-t)\right], & T < T_e \end{array} \right. \]

(8)
where \( t \) is the reduced temperature defined by \( t = T/T_c \). Now we have from Eqs. (6) and (8)

\[
\frac{\rho}{\rho_e} = \frac{1}{t} \left\{ 1 - \frac{2(t-1)}{(k_F d)^2} \log \left[ 1 + \frac{(k_F d)^2}{2(t-1)} \right] \right\}, \quad (T > T_c)
\]

\[
= \frac{1}{t} \left\{ 1 - \frac{4\delta}{(k_F d)^2} \left( 1 + \frac{9}{2} \right) \log \left[ 1 + \frac{(k_F d)^2}{4} \frac{1}{\delta(1+(9/2)\delta)} \right] \right\}, \quad (T < T_c)
\]

in which \( \delta = 1 - t \), and use has been made of \( b = k_B T_e/d \). Equation (9) is plotted in Fig. 1.

Fig. 1. Resistivity vs. temperature curves near the second order transition point \( T_c \) for cases of \( k_F d = 0.4 \) and \( 1.0 \). \( \rho_e \) is the value of \( \rho \) at \( T_c \) and \( t \) is the reduced temperature \( T/T_c \). Figures 1 and 0.4 stand for values of \( k_F d \).

(b) The case of order-disorder phenomena associated with the first order transition such as in \( \text{AB}_3 \) alloy.

In this case we take \( x \) as the long range order parameter \( s \) in order-disorder phenomena.\(^{10}\) In the vicinity of the transition temperature\(^{10}\) we have for \( a = \partial^3 f/\partial x^3 \)

\[
a = k_B T_e \times \left\{ \frac{\alpha + \beta (t-1)}{\alpha' + \beta'(1-t)}, \quad T > T_c \right\}
\]

\[
= k_B T_e \times \left\{ \frac{0.1239 + 1.414 (t-1)}{0.1068 + 6.428 (1-t)}, \quad T < T_c \right\}
\]

Substituting Eq. (10) in Eq. (6) we obtain respectively for \( T > T_c \) and \( T < T_c \),

\[
\frac{\rho}{\rho_e} = 1 + \left\{ 1 + \frac{\beta}{\alpha} \frac{A + (\alpha/4(k_F d)^2) \log A}{1 + (\alpha/4(k_F d)^2) \log A} \right\} (t-1) + \cdots \quad (11a)
\]

\[
\frac{\rho}{\rho_e} = 1 + \left\{ -1 + \frac{\beta'}{\alpha'} \frac{A' + (\alpha'/4(k_F d)^2) \log A'}{1 + (\alpha'/4(k_F d)^2) \log A'} \right\} (1-t) + \cdots \quad (11b)
\]

\[
A = \left[ 1 + \frac{4}{\alpha} (k_F d)^2 \right]^{-1}, \quad A' = \left[ 1 + \frac{4}{\alpha'} (k_F d)^2 \right]^{-1}
\]
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where \( \rho_1 \) and \( \rho' \) are respectively the values of \( \rho \) immediately above and below \( T_c \). In the case of \( k_Fd=0.4 \), Eqs. (11) reduce to

\[
\frac{\rho}{\rho_1} = 1 - 2.35(t - 1), \quad T > T_c \tag{11a'}
\]
\[
= 1.042 - 17.9(1 - t), \quad T < T_c \tag{11b'}
\]

and \( \rho_1 \) is given by

\[
\rho_1 = 0.648 \rho_o, \tag{12}
\]

where use has been made of \( b = k_F^2 T_c / d \), this may be correct in order of magnitude.

On the other hand a simple theory\(^{10}\) predicts \( \rho = \rho_0 \times (1 - s^2) \), \( \rho_0 \) being the constant value of resistivity for \( T > T_c \). Then in the present case of the first order transition there appears a change in \( \rho ; \rho_0 s^2(T_c) \) at \( T_c \), because of a discontinuity \( s(T_c) \) in order parameter. In usual this abrupt change \( \rho_0 s^2(T_c) \) at \( T_c \) is larger than \( 0.042 \rho_1 \) that is the difference between resistivities immediately above and below \( T_c \) (see Eqs. (11a') and (11b')), and so in practice the difference \( 0.042 \rho_1 \) is immaterial.

It is easily seen from Eqs. (11a') and (11b') that the resistivity due to fluctuating parts of the order parameter changes with temperature in proportion to \( |T - T_c| \) near \( T_c \), and that the coefficient of proportionality is much larger in the lower side of \( T_c \) than the one in the upper side, though the respective values of the coefficient are rather meaningless because of approximations employed in the present treatment.

§ 3. Discussions

In § 2 the calculation is based on the results of Landau's phenomenological treatment of fluctuations,\(^7\) i.e. on Eq. (5) whose expression is only applicable to fluctuations of long wave length. Then the present calculation is confined to the case of small \( k_F \) or \( k_Fd < 1 \), since the wave number transfer \( |k' \sim k| \) is less than \( 2k_F \) and the scattering processes with large wave number transfer are most effective in determining resistivity because of the factor \( 1 - \cos \theta \).\(^8\)

In the both cases of the first and second order transitions there appears a peak at \( T_c \) in the resistivity-temperature curve. This is due to the critical scattering of conduction electrons near a transition point. The peak associated with the second order transition is much steeper than that of the first. This is due to the fact that \( a \) does vanish at \( T_c \) in the second order transition but \( a \) does remain finite at \( T_c \) in the first order one. It is worth while to point out that the temperature dependence of \( \rho \) such as in Eq. (9) is a general feature inherent in the second order transition in which \( a \) vanishes at \( T_c \). In reality this is the case for \( \rho \) given by de Gennes and Friedel\(^9\) and by Kim.\(^6\) For example, from Eq. (5·8) of reference 3) one obtains easily in the case of \( k_Fd < 1 \),
which shows the same temperature dependence as Eq. (9) except a dimensionless constant factor of order of unity. Equation (9) or the above expression shows that the peak is prominent in the temperature range \( |T - T_c| / T_c \ll (k_F d)^2 \). It is easily seen from Eq. (9) that the smaller is \( k_F \), the steeper the peak.

In the case of the first order transition the peak at \( T_c \) is less pronounced than in the second order one and is masked partly by resistivities of other causes such as electron-phonon scattering. However it seems to explain a small hump in resistivity-temperature curve observed at \( T_c \) by Nix and Shockley\(^{11}\) for \( \text{Cu}_3\text{Au} \).

References

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