An analysis of short-range order in Ni_3Mn alloy by means of electrical resistivity measurements

1989 J. Phys.: Condens. Matter 1 6327

(http://iopscience.iop.org/0953-8984/1/36/001)

J. Phys.: Condens. Matter 1 (1989) 6327–6333. Printed in the UK

An analysis of short-range order in Ni_3Mn alloy by means of electrical resistivity measurements

G J Stanisz, J Sołtys and J M Holender
Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland

Received 5 July 1988, in final form 7 February 1989

Abstract. The general task of the present work is to test the correlation between experimental resistivity and atomic ordering in alloys. We used the Rossiter model to describe the SRO contribution to the total electrical resistivity. This model allows us to calculate the SRO resistivity at a given temperature as long as the Cowley–Warren parameters are known. The theory of Clapp and Moss has been applied to obtain the Cowley–Warren parameters as functions of temperature and interaction energies of atoms at different distances. Hence, the SRO resistivity could, like the Cowley–Warren parameters, be represented as a function of interaction energies and temperature. To test this model we used experimental resistivity data for Ni_3Mn, and from the total resistivity we obtained the SRO contribution, to which we fitted the model function. From the above calculations we got the values of interaction energies, from which we could obtain the temperature dependencies of the Cowley–Warren parameters.

1. Introduction

Recently, great progress has been made in the theoretical and experimental investigation of transport phenomena in solid solutions. In particular, resistometric studies are very useful for investigations of phase transformation kinetics, examination of short-range-ordering (SRO) processes etc. Because of their simplicity, resistivity measurements are very often used in SRO–kinetics studies, especially to predict the relaxation times and activation energies of the ordering processes. The most recent papers (e.g., Richter and Schubert 1983, Wells and Rossiter 1971, Rossiter 1977) show that electrical resistivity is very sensitive to atomic order. Hence, resistivity measurements could be used to make some preliminary studies for SRO investigations and are complementary to diffraction studies. The general task of the present paper is to test the Rossiter model of SRO resistivity and its applicability to Ni_3Mn alloy.

2. Short-range order in alloys

For the completely disordered binary AB alloy the probability of finding the atom A at any site is equal to the concentration of the atom A in this alloy. However, there are

0953-8984/89/366327 + 07 $02.50

always some correlations. It is very useful to express these correlations using the Cowley–Warren (Cowley 1950) SRO parameters:

$$\alpha_i = 1 - P_i^{BA}/m_A \tag{1}$$

where α_i is the Cowley–Warren parameter of the ith coordination shell, P_i^{BA} is the probability that the site at the ith coordination shell of atom B is occupied by atom A, and m_A is the concentration of atoms A in the alloy. The parameters α_i are very suitable for our purposes because their Fourier transform is simply the scattered intensity measured directly in x-ray or neutron diffuse scattering experiments.

3. The effect of short-range ordering on the electrical resistivity

Electrical resistivity of a pure metal arises from the scattering of conduction electrons by the deviations in the lattice potential periodicity resulting from the existence of impurities, dislocations and phonons. In the binary alloy there are also two additional contributions due to the lack of periodicity in the atomic arrangement arising from the short-range ordering and static atomic displacement. According to Rossiter (1977) it has been shown that, above the critical temperature, T_c (LRO–SRO), this resistivity may be expressed in terms of the Cowley–Warren parameters:

$$R_{SRO} = R_\infty \sum_i c(r_i)\alpha(r_i)Y(2k_F r_i) \tag{2}$$

where R_{SRO} is the order-dependent electrical resistivity at a given temperature, R_∞ is the coefficient denoting the resistivity at high temperatures where the alloy is completely random, $c(r_i)$ is the number of atoms at the ith coordination shell with the radius r_i, $\alpha(r_i)$ is the Cowley–Warren parameter at the ith shell, and $Y(2k_F r_i)$ is defined as follows:

$$Y(2k_F r_i) = \frac{4}{(2k_F)^4}\int_0^{2k_F} \frac{K^3 \sin(Kr_i)}{Kr_i}\,dK \tag{3}$$

where k_F is the Fermi radius.

In (2) we neglect the static atomic displacements because they give only small (within 2%) effects. Formula (2) allows us to predict the value of the order-dependent electrical resistivity at any temperature. To obtain its temperature dependence further assumptions have to be made.

4. The temperature dependence of the Cowley–Warren parameters

Assuming that the Fermi radius k_F and the lattice parameters, as well as the number of conduction electrons (this value is decided by the R_∞ coefficient), are independent of temperature, it is easy to see that the temperature dependence of R_{SRO} is hidden in the Cowley–Warren parameters. According to the theory of Clapp and Moss (1966) we could use the following set of the linear equations:

$$\alpha(r_i) = -2m_A m_B \beta \sum_n V(r_n) \sum_j^{i,n} \alpha(r_j) \tag{4}$$

where m_A and m_B are the concentrations of A and B in the alloy, $\beta = kT$ (k is the

Boltzmann constant, T the temperature), the second summation is carried out over j for sites that are nth neighbours of the ith site, and $V(r_n)$ is the following linear combination of the energies of interaction of pairs of A and B atoms separated by the distance r_n:

$$V(r_n) = \tfrac{1}{2}(V_{AA}(r_n) + V_{BB}(r_n)) - V_{AB}(r_n). \tag{4a}$$

Formula (4), according to Clapp and Moss (1966), can be used only for temperatures higher than 1.1 T_c.

A further assumption has been made: $\alpha(r_i) = 0$ for $i > 6$ (this is quite obvious because the values of the Cowley parameters decrease when the coordination shell number increases. Another reason for imposing a cut-off on the summation at the sixth term is that the function $Y(2k_F r_i)$ oscillates, with the amplitude of the oscillations decreasing very strongly with increasing r_i).

5. Experimental details

To test the above model we have chosen the alloy Ni_3Mn. The SRO processes in this alloy have been investigated by many authors (e.g., Collins and Teh 1973, Beers and Guttman 1974, Orehotsky *et al* 1982, Hatta and Shibuya 1978). The critical temperature has been evaluated as 723 K.

The resistivity was measured in the range of temperature from 1300 K to room temperature with a cooling rate of 0.2 K min^{-1}. We have measured the resistivity for various values of the cooling rate (from 0.1 to 0.5 K min^{-1}), and in all cases we got the same curve for resistivity versus temperature.

Because, the Clapp and Moss (1966) formulae for Cowley parameters used in this paper hold good only for temperatures above 1.1 T_c, the most interesting range of temperatures is that from 1.1 T_c to 1300 K. The cooling rate was fixed at 0.2 K min^{-1} in order to ensure that, in this range, the difference between the measured resistivity and the real equilibrium resistivity is small (about 0.05%). For temperatures near the transition point this error is close to 0.1%.

The results of the experiment are shown in figure 1.

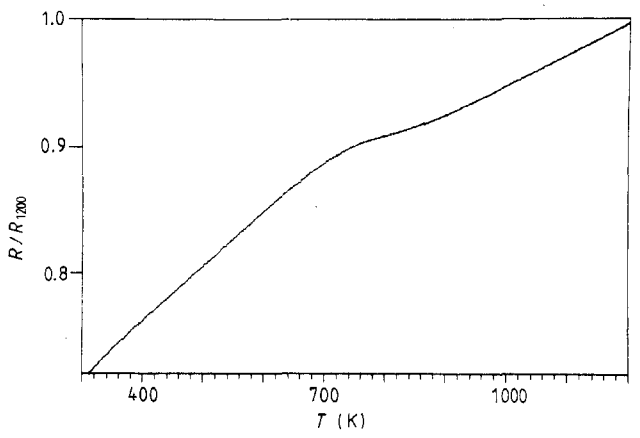

Figure 1. The experimental electrical resistivity of Ni_3Mn. The errors are too small to be marked (see the text).

6. Calculations

Figure 1 shows the electrical resistivity of Ni_3Mn arising from not only the atomic rearrangements caused by SRO but also the phonons, impurities, dislocations etc. Hence, it is necessary to separate these two contributions. We assume that for very high temperatures the SRO contribution to the resistivity is constant. This seems to be the case, because according to (2) R_{SRO} decreases as fast as the Cowley parameters do and in this case (Clapp and Moss 1966) above 1200 K the changes of α_i are very small. Let us define $R_{c,SRO}$ as this approximate value of R_{SRO} above 1200 K. Summing up, above the critical temperature, the total resistivity is given by the following formula:

$$R_{exp}(T) := R_{phonons}(T) + R_{disorder} + R_{SRO}(T). \tag{5}$$

The sum of the first two contributions was assumed to yield a linear function of temperature, because $R_{phonons}$ can be approximated by γT and $R_{disorder}$ is constant. The straight-line parameters were evaluated on the basis of the experimental $R(T)$ dependence at temperature 300 K above the SRO critical temperature. The result of the subtraction is given in figure 2.

Formula (2) was fitted to the experimental data (above the critical temperature), obtained by the above subtraction, as follows. First, the set of linear equations given by formula (4) was solved in two ways:

(i) it was assumed that all the α_i are equal to 0 for $i > 6$ and that $V(r_n)$ is close to zero for $n > 2$;

(ii) it was assumed that all the α_i are equal to 0 for $i > 6$ and that the pair $V(r_n)$ is close to zero for $n > 4$.

The outcome of solving the equations (4) was an expression for the Cowley parameters as functions of temperature and the values of $V(r_n)$ at the nth coordination shell:

$$\alpha_i = \alpha_i(T, V(r_1), V(r_2)) \qquad \text{case (i)}$$

$$\alpha_i = \alpha_i(T, V(r_1), V(r_2), V(r_3), V(r_4)) \qquad \text{case (ii)}.$$

The following functions have been fitted to the experimental data:

$$R_{SRO}(T) = R_\infty \sum_{i=1}^{6} c(r_i) Y(2k_F r_i) \alpha_i(T, V(r_n)) + R_{c,SRO}. \tag{6}$$

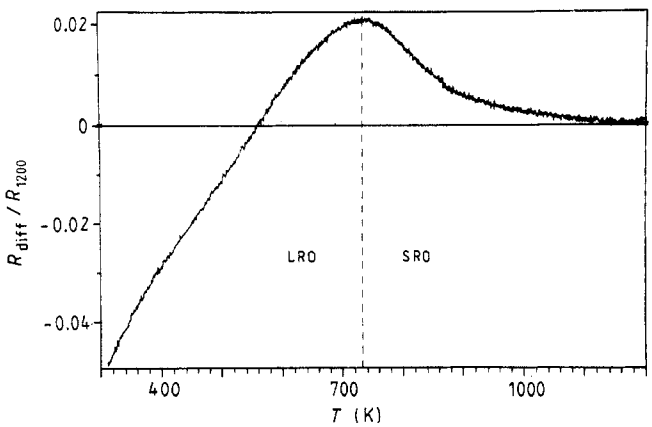

Figure 2. The result of separation of the SRO resistivity from experimental data—R_{diff} (see (5)).

Table 1. The values of the fitted parameters. $V(r_i)$ is given in units of the Boltzmann constant. The Fermi radius k_F is given in units of 10^8 cm^{-1}.

	Case (i)	Case (ii)
$V(r_1)$	410 ± 30	450 ± 20
$V(r_2)$	−72 ± 20	−90 ± 15
$V(r_3)$	—	−20 ± 5
$V(r_4)$	—	8 ± 2
k_F	1.29(2)	1.29(1)

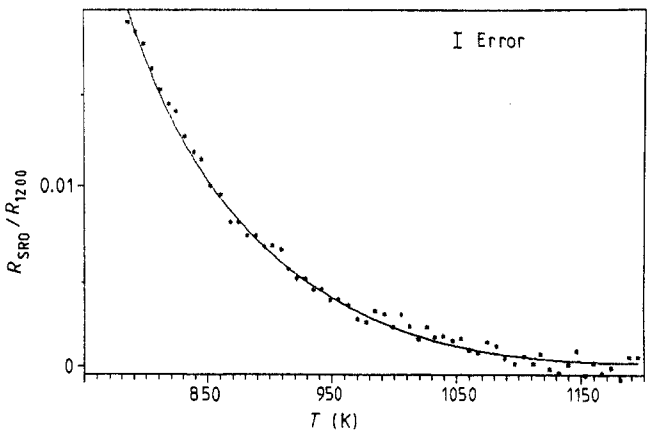

Figure 3. The result of fitting (6) in case (ii) to the SRO contribution (stars). The curve was obtained by fitting.

7. Results

Table 1 and figure 3 present the results from fitting the above formulae. The fitting procedure was repeated several times to estimate the parameter errors. It was shown that procedure (ii) yields a better approximation to the experimental data. Taking into account the terms with α_i ($i > 6$) in formula (2) or using in formula (4) the values of $V(r_n)$ for more than four coordination shells seems to be ineffective because of the unstable results and also because numerical calculations are very time consuming—there are too many parameters to be fitted.

The SRO–LRO critical temperature can be estimated on the Bragg–Williams approximation (Moss and Clapp 1968) using the values obtained for $V(r_n)$:

$$T_c = (3V(r_1)/2k)(1 - \tfrac{3}{2}V(r_2)/V(r_3) + 2V(r_3)/V(r_1) + \ldots). \tag{7}$$

Using the above formula we get $T_c = 800 \pm 50$ K in case (i) and $T_c = 780 \pm 50$ K in case (ii). We can estimate T_c as the temperature corresponding to the maximum of R_{diff} in figure 2. It is 735 ± 5 K.

The value of the Fermi radius obtained from our analysis ($(1.29 \pm 0.02) \times 10^2$ cm^{-1}) is very close to the quantity obtained using simple interpolation of literature data for pure elements.

8. Discussion

The results from the fitting make it possible to get the temperature dependencies of Cowley–Warren parameters from equations (4). The various curves are shown in figure

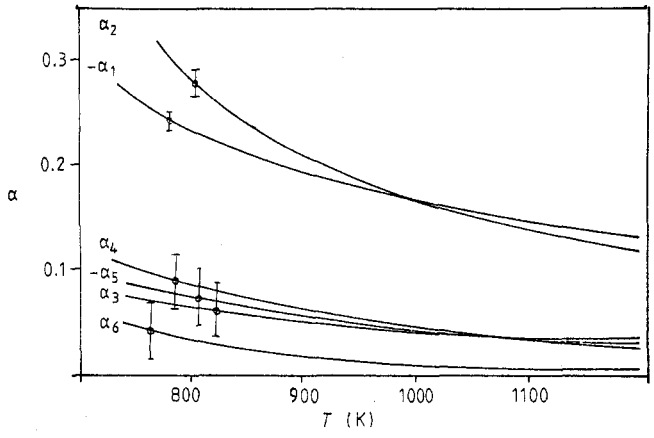

Figure 4. The temperature dependencies of the Cowley–Warren parameters.

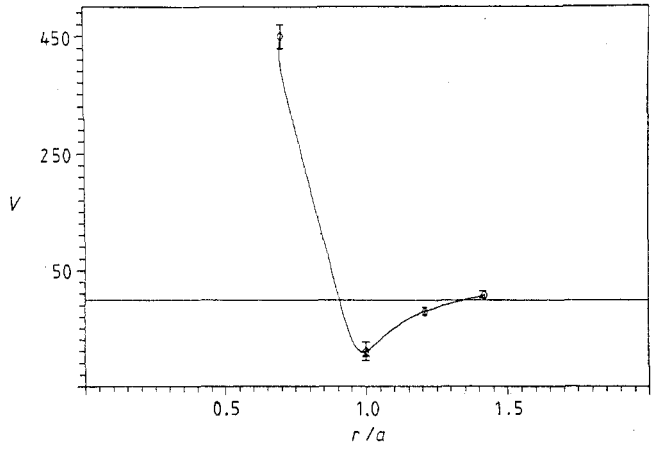

Figure 5. V versus r (in units of the lattice constant). The full curve is only hypothetical.

4. It should be noticed that curves for $i > 2$ are determined with much lower accuracy. There are no literature data to compare the latter dependencies with but it can be seen that their shape is reasonable.

Using the values of $V(r_n)$ derived from procedure (ii) we can construct an approximate plot of V versus r (figure 5). It is obvious that it is impossible to get a satisfactory curve using only four points. Hence this picture should be treated as only a rough representation of the real one.

Analysis of figure 4 and table 1 allows us to draw the following conclusions:

(i) the correlations between the atoms are very high for nearest neighbours and next-nearest neighbours and rather low for higher-coordination spheres;

(ii) the values and signs of α_1, α_2, $V(r_1)$ and $V(r_2)$ indicate that, in the case of Ni_3Mn, atomic ordering rather than clustering occurs; and

(iii) the rather large value of $V(r_2)$ ($\simeq$20% of $V(r_1)$) in contrast to that for Cu_3Au ($\simeq$9%—see Cowley 1950) shows that the interaction between the next-nearest neighbours is extremely strong.

The above model enables us to provide quite a good analysis of short-range order in alloys under conditions where it is possible to separate out different contributions to

the electrical resistivity. This may often be a non-trivial problem, but was relatively straightforward for Ni_3Mn.

Acknowledgments

We would like to thank Dr Rafał Abdank-Kozubski from the Institute of Physics, Jagellonian University, Cracow, for valuable discussions. This present work was supported by Central Program CPBP 01.12.

References

Beers J C and Guttman L 1974 *Phys. Rev.* B **9** 3941
Clapp P C and Moss S C 1966 *Phys. Rev.* **142** 418
Collins M F and Teh H C 1973 *Phys. Rev. Lett.* **30** 781
Cowley L M 1950 *Phys. Rev.* **77** 669
Hatta I and Shibuya M 1978 *J. Phys. Soc. Japan* **45** 487
Moss S C and Clapp P C 1968 *Phys. Rev.* **171** 764
Orehotsky J, Sousa J B and Pinheiro M F 1982 *J. Appl. Phys.* **53** 7939
Richter J and Schubert G 1983 *Phys. Status Solidi* b **116** 597
Rossiter P L 1977 *J. Phys. F: Met. Phys.* **7** 407
Wells P and Rossiter P L 1971 *Phys. Status Solidi* a **4** 151