Physics

I. Ya. Dekhtyar, S. G. Litovchenko, V. S. Mikhalenkov

1962

SovietRxiv

Abstract

Full Text

Physics

I. Ya. Dekhtyar, S. G. Litovchenko, V. S. Mikhalenkov

STUDY OF POSITRON ANNIHILATION WITH ELECTRONS IN ORDERING ALLOYS

(Presented by Academician G. V. Kurdyumov on 8 VI 1962)

The study of changes in the parameters characterizing the states of conduction electrons during the process of alloy ordering is of interest for clarifying the question of the driving forces of this process and the causes of stabilization of the ordered phase. The method of electron–positron annihilation, which has developed in recent years ([1]–[3]), is used for the first time in the present work to study the change in the maximum momenta p_m of conduction electrons during ordering of the alloys Ni_3Mn, Cu_3Au, and CuAu.

The sizes of Ni and Mn atoms are close; therefore, when they are alloyed, elastic stresses caused by differences in atomic sizes do not arise. Conversely, Cu and Au differ greatly in atomic sizes, so that upon alloying large elastic stresses arise, caused by this factor. The alloy Cu_3Au in the ordered state has the same structure as Ni_3Mn. The alloy CuAu differs in structure from the alloys mentioned; in the ordered state it has a layered structure. Thus, the alloys were selected so that they differed both in elastic stresses and in structure.

The alloys were prepared from high-purity metals. Disorder of the alloy Ni_3Mn (23.8 at.% Mn) was achieved by quenching from 800°, and its ordering was achieved by annealing: at 360° for 120 h, and then at 400° for 50 h, with subsequent slow cooling. A single crystal of the Cu_3Au alloy was ordered at 360° for 115 h, and its disordering was achieved by quenching from 900° in water. Polycrystalline specimens of the CuAu alloy were subjected to ordering annealing at 390° for 126 h. Figure 1 presents curves of the angular distribution of annihilation quanta in the ordered and disordered states. As follows from Fig. 1, the annihilation curves for the Cu_3Au alloys in the ordered and disordered states are practically indistinguishable, whereas the Ni_3Mn and CuAu alloys have differing annihilation curves for the disordered and ordered states. It turned out that the values of p_m for the disordered and ordered states of the Cu_3Au alloy are identical and equal to $8.05 \cdot 10^{-3} mc$. For the Ni_3Mn alloy, the value of p_m for the disordered state is $8.52 \cdot 10^{-3} mc$, and for the ordered state $8.04 \cdot 10^{-3} mc$, i.e., about 6% smaller.

In the CuAu alloy the values of p_m for the states studied also turn out to be different. For the ordered state the value of the maximum momentum is

Figure 1: Angular distribution of annihilation photons for Ni_3Mn and Cu_3Au alloys.

Figure 1: Figure 1: Angular distribution of annihilation photons for Ni_3Mn and Cu_3Au alloys.

$8.0 \cdot 10^{-3} mc$, and for the disordered state $8.9 \cdot 10^{-3} mc$*. In this case the difference is about 11%.

Thus, in some cases the value of p_m does not change upon ordering of the alloy (Cu_3Au), while in others it decreases (Ni_3Mn and CuAu). In alloys of the CuAu type the ordered phase is characterized by a layered dis–

* The values of the maximum electron momenta are given in mc units. To convert them to the CGS system ($g \cdot cm/sec$), it is necessary to multiply p_m by the value $mc = 2.9 \cdot 10^{-17}$ $g \cdot cm/sec$.

arrangement of atoms of different kinds. Conversely, in alloys of the Cu_3Au, Ni_3Mn type, the ordered structure is characterized by an arrangement of atoms in which an atom of one kind tends to surround itself with atoms of another kind. In some cases an atom of each kind is surrounded by an equal number of atoms of both kinds. Thus, the usual explanation of the phenomenon of ordering, given by Hume-Rothery and treating this phenomenon as a process in which an atom of one kind tends to surround itself with atoms of another kind because this produces the maximum

Fig. 1. Angular distribution of annihilation photons for the alloys Ni_3Mn and Cu_3Au. *a* –disordered state, *b* –ordered state

decrease in the energy of lattice distortions caused by the difference in atomic sizes, apparently is not always justified and is incomplete.

In the work of A. A. Smirnov[4], the possibility is indicated, in some cases, of splitting the Brillouin zone into two halves in a lattice with a doubled periodicity of the potential. In this case such a change in the energy levels occurs that, if the zone was half filled with electrons, the energy of the electrons decreases by an amount proportional to S^2, where S is the degree of long-range order. Such a decrease in the electron energy may be one of the causes stabilizing the ordered phase. In Fig. 2 the dependence $E(k)$ is shown schematically in the absence of a perturbing potential and in a perturbed potential field. If the number of electrons is sufficient to fill half of the ordinary zone, then, in the presence of a perturbing potential, they fill the lower half of the zone, leaving an energy gap in the upper half. In this case the electron energy of the occupied levels at the top of the lower subzone is lowered, which, according to Slater, leads to stabilization of the ordered state. Quantitatively, the decrease in the mean energy is proportional to the square of the width of the energy gap divided by the electron energy at the edge of the gap. Since the width of the energy gap is proportional to the degree of long-range order, the decrease in the energy of the

Fig. 2. Schematic representation of the distribution of energies over momenta in the band. *a*—disordered state, *b*—ordered state

Figure 2: Fig. 2. Schematic representation of the distribution of energies over momenta in the band. *a*—disordered state, *b*—ordered state

electron system must be proportional to the square of the degree of long-range order. For an alloy in whose ordered phase the case shown in Fig. 2b is realized, it may be assumed that the decrease in the mean energy of the electrons, caused by the lowering of the energy levels at the top of the lower subzone, should lead to a corresponding lowering of the Fermi energy.

The curves of the angular distribution of annihilation quanta, according to (1), can be transformed into curves showing the dependences $N(p)$, i.e., giving information on the distribution of electrons over momenta.

The change in the shape of the curves $N(p)$ upon ordering of the alloy should be reflected, first of all, in a decrease in the maximum electron momentum, which corresponds to a compression of the energy levels when an energy gap is formed (Fig. 2b). Secondly, the value of $N_{\max}(p)$ should be larger for the ordered state, since the total number of occupied energy levels, characterized by the area bounded by the curve $N(p)$, must remain unchanged. The total energy of the system may be represented as the sum of the energies of the atomic cores and the kinetic energy of the electrons. Considering the change in free energy at room temperature, one may, in a first approximation, neglect the change in entropy and, similarly to how Jones ([5]) considered the change in Fermi energy upon stabilization of the α- or β-phase in brass due to a change in electron concentration, consider the change in the mean kinetic energy of the electrons caused by a change in the degree of long-range order.

Fig. 2. Schematic representation of the distribution of energies over momenta in the band.
a—disordered state, *b*—ordered state

Assuming that the transition from one state to another is not accompanied by a change in electron concentration, the above condition may be written as follows:

$$n = \int_0^{p_{ym}} N_y(p)\,dp = \int_0^{p_{hm}} N_h(p)\,dp, \tag{1}$$

where $N(p)$ is the number of electron states having momenta in the interval $p \div p + dp$. The total momentum of the electrons in an ordered alloy is expressed by the relation

$$P_y = \int_0^{p_{ym}} pN_y(p)\,dp, \tag{2}$$

and for the disordered state

$$P_h = \int_0^{p_{hm}} pN_h(p)\,dp. \tag{3}$$

The total energy of the electrons for these states can be expressed as follows:

$$W_y = P_y^2/2m, \qquad W_h = P_h^2/2m. \tag{4}$$

Then the change in the energy of the system upon transition from the disordered state to the ordered state will be

$$\Delta W = W_h - W_y. \tag{5}$$

In this case one may consider two cases: 1) $\Delta W \approx 0$ and 2) $\Delta W > 0$. In the first case, stabilization of the ordered phase is caused not by a change in the Fermi energy but, most likely, by a change in the energy of lattice distortions determined by the difference in the sizes of the atoms of the components. If the second case is realized, then the stabilization of the ordered state is caused by a change in the Fermi energy of the electrons.

As was shown in work ([1]), the density of states can be related to the angular-correlation curve of the annihilation photons by the relation

$$N(p) = 4\pi p^2 \rho(p) = \text{const}\,\frac{dI(z)}{dz}\,z = \beta\,\frac{dI(p)}{dp}\,p, \tag{6}$$

where $\rho(p)$ is the density of states; z is the deviation, expressed in millimeters, of the annihilation photons from collinearity; $I(z)$ is the counting rate of coincident pulses.

The deviation z is related to the photon momentum

$$p_z = \frac{2mc}{d}\,z = \chi z, \tag{7}$$

where d is the distance from the counter to the axis of the positron source; p_z is the vertical component of the electron momentum; m is the mass; c is the speed of light. We note that in all the preceding formulas p must be understood as the z-component of the momentum, measured in the experiment. Thus, the integrand in formulas (2) and (3) can be written in the form

$$pN(p)\,dp = p\beta\frac{dI}{dp}\,p\,dp = \beta p^2 dI. \tag{8}$$

For the parabolic part of the annihilation curve, according to (2) we have

$$I(p_z) = a(p_z^2 - p_m^2), \tag{9}$$

where a is a constant. Consequently, $dI = 2ap\,dp$. Using this relation and carrying out the integration in formulas (2) and (3), we obtain

$$P_{\text{y}} = \frac{2}{3}(\beta a)_{\text{y}} p_{\text{y}m}^4, \qquad P_{\text{n}} = \frac{2}{3}(\beta a)_{\text{n}} p_{\text{n}m}^4. \tag{10}$$

Thus, the condition for stabilization of the ordered state may be the relation

$$P_{\text{y}} < P_{\text{n}} \quad \text{or} \quad [(\beta a)_{\text{y}} p_{\text{y}m}^4] < [(\beta a)_{\text{n}} p_{\text{n}m}^4]. \tag{11}$$

In the alloy Cu_3Au the annihilation curve does not change upon ordering. Consequently, the values of p_m also remain unchanged. This fact indicates that ordering in the Cu_3Au alloy is not accompanied by the formation of an energy gap and a depression of the electron levels in the lower subzone. At the same time, the atoms of the components in the alloy have strongly differing sizes ($d_{\text{Cu}} = 2.55$; $d_{\text{Au}} = 2.88$ Å). Evidently, the cause of stabilization of the ordered phase in this alloy is the decrease in the energy of distortion of the crystal lattice when the atoms are arranged in an ordered manner.

In the CuAu alloy, the ordering process is accompanied by a decrease in the value of p_m. In addition, the atoms of the components differ sharply in their sizes. However, in contrast to the Cu_3Au alloy, ordering here is not accompanied by the formation of such a structure in which atoms of one kind tend to surround themselves with atoms of another kind—a structure that favors the maximum reduction of elastic stresses. The ordered structure of the CuAu alloy is characterized by a layered arrangement of atoms, which indicates that, in the stabilization of the ordered phase, the relief of elastic stresses apparently plays a secondary role. The decrease in the Fermi energy evidently has the principal significance.

The alloy Ni_3Mn is characterized by almost identical sizes of the atoms of the components. Therefore, elastic stresses caused by the difference in atomic sizes are absent in this alloy. The results obtained indicate a decrease in the maximum momentum of the electrons upon ordering of the alloy. Consequently, this cause may play a role in the stabilization of the ordered phase. In addition, upon ordering of the Ni_3Mn alloy, a redistribution of s- and d-electrons occurs, which is expressed in a considerable increase in the saturation magnetization. Apparently, this cause also has significance for the stabilization of the ordered phase [6].

Institute of Metallophysics
Academy of Sciences of the Ukrainian SSR

Received
4 VI 1962

REFERENCES

1. A. T. Stewart, *Canad. J. Phys.*, **35**, 168 (1957).
2. I. Ya. Dekhtyar, V. S. Mikhalenko, DAN, **133**, 60 (1960).
3. I. Ya. Dekhtyar, V. S. Mikhalenko, DAN, **136**, 63 (1961).
4. A. A. Smirnov, ZhETF, **17**, 730 (1947).
5. H. Jones, *Proc. Phys. Soc.*, **49**, 243 (1937).
6. V. M. Danilenko, A. A. Smirnov, *Fiz. met. i metalloved.*, **14**, No. 5 (1962).

Note: Figure translations are in progress. See original paper for figures.