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To the Problem of the Influence of the Spontaneous Magnetization on the Crystal Structure and the Phase State of Alloys

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When two processes—the magnetic transformation and the atomic order-disorder of a solid solution—are superimposed and when the leading part belongs to the first process, there are anomalies in the temperature dependence of the degree of the atomic order, the magnetization and other parameters. This problem is examined in the limits of Bragg-Williams's and Rosing-Weiss's approximations. The analysis of the experimental results of the investigation of the whole series of alloys shows that the 3*d*-exchange interaction can lead not only to the distortion of the solubility limits in one direction or another or to the change of the crystal lattice parameters but also to the formation of the superstructures of ferromagnetic nature. The corresponding supposition had been done for some systems too.

1. The elementary theory of the atomicferromagnetic order-disorder (a. f. o.) in Bragg-Williams's approximation

If the Curie point of a solid solution lies in the region where the atomic diffusion mobility is large enough, it makes possible to superimpose two processes—the magnetic transformation and the atomic order-disorder. To solve this problem exactly in general way it is necessary to calculate reciprocal potentials and the exchange interaction of the components¹⁾. However, for some solid solutions the 3*d*-exchange part of order-disorder energy is apparently predominating^{2),8)}. The spontaneous magnetization and the atomic order-disorder are examined in intercorrelation when the leading part belongs to the first process. In accordance with Rosing-Weiss's and Bragg-Williams's theories the order-disorder energy is equal to

$$U_0(T)\sigma = (A_1y_1^2 - A_2y_2^2)\sigma$$
,

where σ is the parameter of the long range order, A is the exchange parameter, y is the relative magnetization for the ordered (1) and disordered (2) phases. When $T_c \leq \theta_2 \leq \theta_1$ (T_c is the critical point of the order-disorder, θ_1 and θ_2 are the Curie points for the ordered (1) and disordered (2) phases),

$$U_0(T)\sigma \simeq \Delta A(1+T^2/\theta_1\theta_2)\sigma$$

This is Ni₃Fe-type of the atomic-ferromagnetic order-disorder (a.f.o.-I). In this case the energy of the order-disorder has a maximum with the upper limit~1.1 ΔA in the region of $0 < T < T_c$.

When $\theta_2 \ll T_c \leq \theta_1$, $U_0(T)\sigma \simeq A_1(1-T^2/\theta_1^2)\sigma$.

This is Ni₃Mn-type (a.f.o.-II). The general form of $\sigma(T)$ dependence and the correspond-



Fig. 1.

ing equations for two a.f.o. types and for the transition of the second kind are shown in Fig. 1. When U_0 does not depend on T(a=b=0), both a.f.o. types transform in Bragg-Williams's type.

For the a.f.o.-II and the order-disorder transition of the first kind there is the effective Curie point $\theta_2^* \sim T_c$ that corresponds to some critical degree of the short or long range a.f.o. which arises spasmodicly when $T=T_c$. For the a.f.o. of the short range type the point of the beginning of this process coincides with the virtual Curie point θ_1 . The experimentally determined Curie point θ_2 has a characteristic dispersion. A relative magnetization has a specific behaviour too. The reproduction of the shape of the concentration dependences of θ_1 and θ_2 (exactly, their difference) by the some dependence of T_c is also an important peculiarity of the a.f.o. near a stoichiometric composition.

2. Comparison with an experiment

The comparison of the amount of the orderdisorder transition energy Q with the change of the ferromagnetic energy ΔE must be one of the fundamental methods of the diagnostics of the a.f.o. The amount ΔE can be evaluated in accordance with the formula $\Delta E \approx k \Delta \theta/2$ where $\Delta \theta = \theta_1 - \theta_2$. The known results for some superstructures which are likely to be attributed to above mentioned a.f.o. types (with an exception of Fe₃Al) are shown in Table I. For Fe₃Al amounts of Q and ΔE have the opposite signs because spontaneous magnetization counteracts to the atomic orderdisorder¹⁾. When $T \approx T_c \sqrt{\Delta A/Q_{T_c}}$ the orderdisorder process had to be omitted. The diagram of the phase equilibrium of Fe₃A1 has really a shape of (-type in that region where the ferromagnetism is stronger (see

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Superstructure	A.f.o. -type	T _c (°C)	Q (ev/at.)	$\begin{pmatrix} \theta_2 \\ (^{\circ}C) \end{pmatrix}$	$ \begin{pmatrix} \theta_1 \\ (^{\circ}C) \end{pmatrix} $	$\Delta E = k \Delta \theta / 2$ (ev/at.)	$\theta_1^{\max} (^{\circ}C) \text{ from} \\ \Delta E = Q$
Ni ₃ Fe (77.8%Ni)	I		att dates	560 5)	> 590 5)	>1.3.10-3	Braze-Williams's
— " — (75% Ni)	08 10	530 2)	$3.3 \cdot 10^{-2}$ 4)	t percit	sail main		If the Curic mint
— " —(68.8%Ni)		Let Date	and a second second	600 6)	>801 7)	$> 8.7 \cdot 10^{-3}$	1,360
FeCo	I	730 8)	5.0.10-2 8)	~1120 9)	oldiagon		2,280
$Ni_{3}Fe_{1/2}Mn_{1/2}$	I–II	600 10)	5.1.10-2 10)	340 10)	>570 10)	$> 1.0 \cdot 10^{-2}$	1,520
Ni ₃ Mn	II	600 10)	3.2.10-2 10)	~-200 10)	>480 10)	$>2.9 \cdot 10^{-2}$	540
Fe ₃ A1	III	560 6)	$\sim 3 \cdot 10^{-2} 6)$	> 520 6)	<480 6)	$> -2 \cdot 10^{-3} $	lo solve tins problem

Fig. 2). The temperature dependences of y and σ of the alloys—Fe₃Al¹¹), FeCo^{9),12}, Ni₃Fe^{6),2)} and Ni₃Mn (it is evaluated from the temperature dependences of B_s and Q^{13})—are given in Fig. 3. For all dependences typical deviations predicted by the a.f.o. theory are observed.



The specific phenomena during the atomic order-disorder transition of the magnetic solid solutions (a.f.o.) can be generally explained by the shape of Bethe's curve for the exchange energy. So when the superstructures Ni₃Fe, Ni₃Mn, FeCo and others are formed, the essential increase of the distance between the atoms (the bearers of the greatest magnetic moment) takes place. As a result image of the 3*d*-exchange energy of the alloys on Bethe's curve begins to move towards the maximum and the free energy of the alloy decreases on the amount of Q. This point of view can be also applied to the corresponding triple alloys where a part of the atoms of the "left" element (for example: Fe) is replaced by the other "left" element (the antiferromagnetic elements Cr and Mn) or a part of "right" element is substituted by the other "right" element (for example: $Co_{\overrightarrow{c}}Ni$). This examination permits us to make a severe classification of a big group of the superstructures and of stratifications in the magnetic alloys.

The binary superstructures of Ni₃Fe, FeCo, presumably Co₃Mn and Co₃Cr and some triple superstructures of Ni₃(Fe, X), (Ni, X)₃Fe and other types form the I-st type of the a.f.o. The binary superstructures of Ni₃Mn, Pt₃Cr, Pt₃Mn, Pd₃Mn, Au₃Mn, presumably Cu₃Mn, Fe₃Mn and Ag₃Mn and some triple superstructures of Ni₃(Mn,X), (Ni,X)₃Mn and other types form the II-nd type of the a.f.o. The III-rd type of the a.f.o. is formed by superstructures of Fe₃Al type ($\theta_1 < \theta_2 \ge T_c$, case IIIa) while the leading part in the a.f.o. process belongs to the atomic order-disorder process (Fe₃Al, Fe₃Si, CoPt, NiPt), and by a negative order-disorder types ($\theta_2 < \theta_1 \ge T_c$, case IIIb): the solid solutions Fe-Cr, Fe-V, Fe-Ni (invar compositions), Ni-Au, Ni-Pd and presumably Co-Ni.

The results of the a.f.o. theory are confirmed for all enumerated systems. The exceptions are the superstructures of FePt and FePd. However, the order-disorder transition



Fig. 3.

in these systems is apparently accompanied by an essential change of the electron structure of the Pt atoms.

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Magnetic Disorder as a First Order Phase Transition

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It is shown that if the exchange interaction (or Curie temperature) of a ferromagnetic depends sufficiently strongly on interatomic distance and the lattice is sufficiently compressible then the ferromagnetic to paramagnetic transition may be of first order, with an associated latent heat and discontinuous density change, rather than of the usual second-order type. This treatment can account for the magnetic transition in MnAs, and is believed to be applicable to other systems.

To view the physics of our treatment, let us consider the usual method of treating magnetic disorder, in which there is assumed to be a ferromagnetic interaction between the magnetic moments localized on each atom site, and in which it is further assumed, usually implicitly, that this interaction is not a function of lattice spacing. At low temperatures there exists substantially complete magnetization or perfect long range order. As the temperature is raised, the thermal randomization tends to destroy this order and the magnetization falls. The course of the magnetization is described more or less by application of the molecualr field concept to the Brillouin function, and at the Curie temperature, T_c , the spontaneous magnetization becomes zero without discontinuity. This transformation is of second order, and the cooperative nature of the system is reflected by a discontinuity in the specific heat at T_c . There is not, however, the latent heat or discontinuous density change that characterize a first-order transition.

Now let us consider what results if we assume that the exchange energy (or Curie temperature) is a strong function of interatomic spacing. We show such a dependence in Fig. 1(a). At absolute zero, the system's free energy may be lowered by distortion of the lattice in the direction of increasing the Curie temperature. This distortion will introduce into the free energy a term in strain energy which will increase the free energy, and thus, a compromise between distortion and exchange may be found that minimizes