

Memorandum M-1929

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SUBJECT: AD HOC CONFERENCE ON FeNi₃

To: David R. Brown

From: D. A. Buck, J. B. Goodenough, A. L. Loeb, N. Menyuk

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Abstract: The undersigned continued the discussion on FeNi₃ initiated by Dudley Buck at the seminar on magnetism, the meaning of order-disorder and entropy were examined. Hysteresis loops, saturation magnetization and Curie point of ordered and disordered states were contrasted, and their differences tentatively explained.

Equilibrium occurs when the free energy A of a system is a minimum. The free energy is related to the internal energy (E), absolute temperature (T) and entropy (S) by the expression $A = E - TS$.

Entropy is interpreted physically as an expression of the randomness" of a system. An alloy with some regions appreciably richer in one constituent than other regions has a low entropy; a completely random distribution does not show a preference for some regions over others.

It should be recalled that entropy is a thermodynamic quantity with a statistical interpretation. A discussion based on entropy therefore necessarily includes a large number of atoms (ions). Order and disorder may be defined for a region of a sample that contains enough atoms (ions) to allow statistical treatment. If the region thus considered contains more than one component the geometrical distribution of the various components can be described by the probability of finding a particular component at any given location in this region. Thus a probability function is assigned to every component. If the probability functions of all components are uniform throughout the region, the region is disordered. If the probability functions of at least one component varies strongly with position, and if the probability functions of the various components are strongly interdependent, the region is ordered. It is plain that a disordered region has a higher entropy than an ordered one.

From the expression for free energy, it can be concluded that at high temperature the entropy accounts for a relatively larger portion of the free energy than at low temperature. The internal energy of an ordered alloy is lower than that of a disordered one, so that one would expect disorder to prevail at high temperature, order at low temperature. For 79% Ni - 17% Fe the transition from ordered to disordered states occurs at 510°C. Below this temperature both ordered and disordered states may exist, though the ordered one has the lower free energy and is therefore stabler. The disordered state can exist in a rapidly quenched specimen because at relatively low temperatures ions and atoms are frozen in their positions and haven't sufficient thermal energy to rearrange themselves. Annealing the alloy (slightly below the transition temperature, for instance

at 490°C) provides the necessary thermal energy for the disordered alloy to order. This process may start locally, with many small regions being internally ordered as defined above, but with no correlation between the various probability functions in different regions. The fact that there are several regions within a sample with different ordering properties indicates that the entropy of such a short range ordered alloy may be quite low. Ferromagnetic states are highly ordered and therefore have a low entropy.

Face-centered cubic FeNi_3 has eight Fe-s at the corners of a cube (hence one Fe per unit cell) and six Ni-s at the centers of the faces (hence three Ni-s per unit cell). In the ordered state the Fe-s are farther apart than the Ni-s and also farther apart than in pure Fe.

Since Ni-Ni interaction leads to ferromagnetic coupling, and Fe-Fe to antiferromagnetic coupling, ferromagnetism prevails when the Ni-s are closer together than the Fe-s.

In terms of the Zener model the Ni ($3d^9$) tends to annex additional electrons to fill up its d-shell, so that the Fe-s carry the uncanceled spins (See "Seminar on Magnetism" LXIV). Since the Fe-s are far apart, s-d coupling prevails over d-d coupling, so that the material is ferromagnetic, while in pure Fe the d-d coupling prevails, causing ferrimagnetism.

In the disordered alloy any Fe-Fe near neighbors couple strongly antiferromagnetically, so some spins are canceled. In the disordered alloy the possibility of Fe-Fe near neighbors is greater than in the ordered one. The saturation magnetization is less for disordered alloys than for ordered ones. This is borne out by the results reported by S. Kaya at the Conference on Magnetism in Washington, September 1952. Since in a 17% disordered Fe alloy the possibility of Fe-Fe near neighbors is still very small, the increase in magnetization with ordering is not expected to be great. Indeed, S. Kaya reported only 4% increase. The partially ordered state (short range order, large range disorder) presents an interesting hysteresis loop. The ordered state is strongly anisotropic, and the hysteresis loop for the ordered, single crystal is correspondingly square. A partially ordered sample may contain many regions with randomly oriented axes, so that the overall sample is isotropic. Imposition of a field might orient these axes, so that two hysteresis processes are superimposed, namely that of orientation of spins within each region, and that of orientation of the various regions.

On ordering B_r/B_m had a minimum, H_c a maximum, at about 5 hours anneal. This corresponds to partial ordering, i.e. ordering in independent clusters. It also represents the condition of the specimen at which the peculiar hysteresis loop characteristics appeared. The regions of order are analogous to different grains in a polycrystalline material. The coercive force will be a maximum when there are a maximum number of these ordered clusters. The ratio B_r/B_m will have a minimum when the number of ordered clusters which are large enough to contain domains of reverse magnetization is a maximum.

Ordered FeNi_3 has a higher Curie point than disordered FeNi_3 . This is explained on the basis of the Zener model. In the ordered alloy

ions with large spins in their d-shell are farther apart than in the disordered alloy. In this case d-d coupling is a minimum and s-d coupling is favored; parallel alignment with a high Curie point results. The same reasoning applies to $MnNi_3$, where the disordered alloy is paramagnetic at room temperature because of Mn-Mn near neighbor coupling. In the ordered $MnNi_3$, as in the Heusler alloys, the Mn-Mn distance is sufficiently large to allow s-d coupling to predominate. Ordered $MnNi_3$ is ferromagnetic.

It would be very interesting to compare also ordered and disordered $FeMn_3$. The electronic structure of this alloy would approximate $Fe^{-3}(3d^{10})Mn_3^{+1}(3d^5)$. In this case the spin would be located on the Mn, and disordering would strongly increase the chances of great proximity of Mn. Even in the ordered alloy the Mn-Mn distances might be small enough to make the Curie point relatively low, but disordering would certainly decrease the Curie point appreciably.

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