Neutron Diffraction Studies of Order-Disorder in Alloys*

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Neutron diffraction techniques have been used to study order in the substitutional solid solutions FeCo, Ni_3Mn, and Cu_3Au. Superlattice effects have been found in the first two examples, which are difficult to study by x-rays.

INTRODUCTION

MANY alloy systems contain substitutional solid solution areas in which an atom A of one constituent merely substitutes at random for an atom B of the other species on the available sites of the lattice. When this substitution is random, the system is described as a disordered solid solution. In some systems, by suitable thermal treatment such a structure can be transformed into an ordered solid solution or superlattice, in which the A atoms are preferentially located with respect to neighboring B atoms, but still on the same lattice sites occupied in the disordered states. X-ray diffraction studies have been extremely instructive in revealing the facts of superlattice formation in such alloys.

A simple example of the order-disorder effects is shown in Fig. 1 for an AB alloy containing equal atomic percentages of the two atoms and crystallizing in a body-centered cubic structure. In the disordered state, B atoms have merely substituted at random for A atoms, whereas in the ordered state there are discrete planes of A atoms and discrete planes of B atoms.

Transformations from a disordered to an ordered state can be studied directly by x-ray diffraction techniques and indirectly by resistivity, specific heat, etc., measurements. Excellent reviews[1] of work performed in this field have been given by Nix and Shockley and by Barrett. The sensitivity of the x-ray diffraction method in detecting such changes depends upon the difference in scattering power of the atoms involved in the structure. Since this difference becomes unfavorably small in certain applications (in FeCo, for instance), it was thought that neutron diffraction techniques might usefully supplement the x-ray procedures. Neutron scattering cross sections do not vary as regularly or in the same manner as x-ray scattering cross sections; hence there are cases where the necessary differences are obtained with one technique and not with the other. This was recognized in early studies of neutron scattering from samples of ordered and disordered alloys by Nix, Beyer, and Dunning.[2] These investigators measured the change in transmission of Fe-Ni samples for a heterogeneous neutron beam obtained from a Ra-Be source. The experimental conditions under which these studies were performed were of necessity rather crude because of the very limited neutron intensity available at that time. Differences were obtained, however, in the transmission by samples of different heat treatment, and these were ascribed to the ordering of the lattice in certain cases.

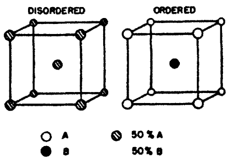

FIG. 1. Typical structure showing order-disorder effects for an alloy AB.

The two structures illustrated in Fig. 1 will produce markedly different diffraction patterns. A pattern characteristic of a simple body-centered cubic lattice and containing reflections (110), (200), (211), (220), (310), etc., will be obtained for the disordered sample while the ordered sample will show not only all of these reflections but the extra ones (100), (111), (210), (300) as well. In its simplest form then, the detection of superstructure is merely to search for the presence of the extra superstructure lines and the ease with which this can be done depends upon the relative intensities of the superstructure lines and the normal lattice lines.

In the Debye-Scherrer-Hull powder technique the intensity in a diffraction line (hkl) as obtained from a powder briquet plate is given by

$$I_{hkl}=\kappa(j_{hkl}F_{hkl}^2/\sin^2 2\ {}_{hkl}), \tag{1}$$

where j_{hkl} is the multiplicity factor, F_{hkl} is the structure factor, θ_{hkl} the Bragg angle of scattering for the (hkl) reflection, and κ is a constant. For a completely disordered sample of AB having the structure shown in Fig. 1

$$F_{hkl}=f_A+f_B \tag{2}$$

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[1] F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938). C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1943), Chapter XII.

[2] F. C. Nix, H. G. Beyer, and J. R. Dunning, Phys. Rev. **58**, 1031 (1940).

TABLE I. X-ray and neutron scattering amplitudes for various atoms.

	X-rays ($\sin\theta/\lambda = 0.2$)	Neutrons
Mn	$4.17 \cdot 10^{-12}$ cm	$-0.32 \cdot 10^{-12}$ cm
Fe	4.33	+0.91
Co	4.54	+0.37
Ni	4.74	+1.04
Ni^{58}	4.74	+1.41
Ni^{60}	4.74	+0.3
Cu	4.95	+0.76
Au	14.90	+0.77

TABLE II. Relative diffraction line intensities characterizing order and disorder in FeCo.

	X-rays	Neutrons
I_{100}	1	1
I_{110}	1390	6.0

per AB molecule, whereas for the ordered sample the structure factors of the extra superstructure lines will be

$$F_{hkl}^{ss} = f_A - f_B \tag{3}$$

and the structure factors for the normal b.c.c. reflections from the ordered sample will be the same as (2). In these expressions f_A represents the scattering amplitude for an atomic center A. It is of interest to compare the scattering amplitudes for the x-ray and neutron cases and some typical values of use in the present studies are shown in Table I.

The x-ray scattering amplitudes vary in a regular fashion approximately as the atomic number and show a pronounced angular variation (form factor). For this reason they are shown evaluated at the angle corresponding to $(\sin\theta)/\lambda = 0.2$. In contrast, the neutron scattering amplitudes show no regular variation with atomic number and are, moreover, independent of scattering angle since the scattering of slow neutrons is isotropic. The neutron wavelength (~1A) is much larger than the dimensions of the scattering nucleus (~10^{-4}A) and this results in isotropic scattering. The signs of the scattering amplitudes for the neutron case are generally positive but sometimes negative as in the case of manganese. For the x-ray case these are invariably positive except in the close vicinity of an absorption resonance when intermediate phases of scattering may be encountered. It is to be noted that different isotopes of the same element can possess drastically different neutron scattering properties, whereas this difference would not be present with x-rays.

The scattering amplitudes given in Table I can be used to compare the relative usefulness of x-ray or neutron diffraction in establishing the presence of superstructure. In illustrating this, the case of FeCo which crystallizes in a structure of the type shown in Fig. 1 will be used. Table II compares the intensities to be expected for the (100) superstructure reflection and the (110) normal lattice reflection for the two cases. These have been calculated using the x-ray amplitudes and scattering angles obtained with CoKα x-radiation and with a neutron wave-length of 1.06A. Suitable substitution in Eq. (1) provides the relative intensities. From these calculated values it is seen that neutron scattering techniques would be much more sensitive for the detection of structural order. For other systems, the reverse may be true, depending upon the relative amplitudes of scattering for the constituent atoms.

Jones and Sykes[3] have extended the usefulness of the x-ray technique in these unfavorable cases by taking advantage of the anomaly in x-ray scattering power for radiation of wave-length near to that of an absorption edge. Thus when copper atoms are irradiated by ZnKα x-rays, the x-ray scattering amplitude is altered somewhat from its normal value and this may assist in establishing the presence of order in a copper alloy. They were able to show by this procedure that β-brass (CuZn) did exist in an ordered state at room temperature. Likewise, Ellis and Greiner[4] have shown the ordering which can be produced in FeCo.

EXPERIMENTAL RESULTS

For initial study, the three alloys FeCo, Ni_3Mn, and Cu_3Au appeared to possess exemplary scattering properties. The former two are extremely difficult to study with x-radiation for reasons discussed above, while the latter is quite amenable to x-ray techniques and has been extensively investigated. Details of the neutron diffraction techniques have been given in the literature[5] so these will not be discussed here. A monochromatic beam of neutrons (wave-length 1.06A) was diffracted by samples of loose powder held in position by parallel windows of thin aluminum. The powder diffraction pattern was obtained by counting the number of scattered neutrons at various angular positions of the detecting counter. The neutron counting rate

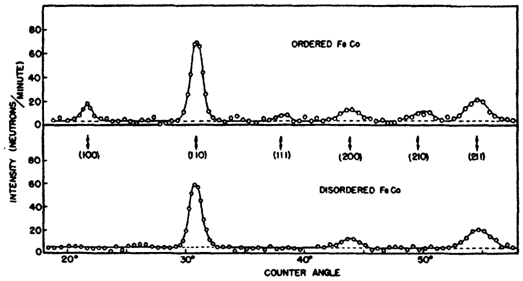

FIG. 2. Neutron diffraction patterns for ordered and disordered samples of FeCo.

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[3] F. W. Jones and C. Sykes, Proc. Roy. Soc. **161**, 440 (1937).

[4] W. E. Ellis and E. S. Greiner, Trans. Am. Soc. Metals **29**, 415 (1941).

[5] E. O. Wollan and C. G. Shull, Phys. Rev. **73**, 830 (1948).

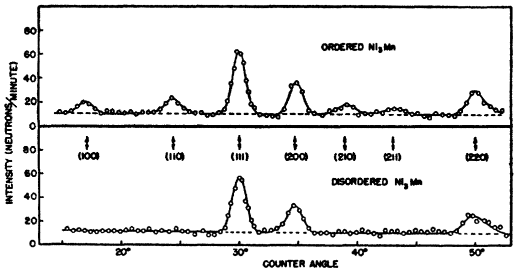

FIG. 3. Neutron diffraction patterns for ordered and disordered samples of Ni_3Mn.

in the diffraction pattern was, at most, of the order of one neutron per second and, since this is only about five times normal counter background, it was necessary to scan the pattern a number of times to smooth out statistical fluctuations. All of the data have been corrected for counter background.

Figure 2 shows the patterns obtained for ordered and disordered samples of FeCo. The disordered sample had been quenched in water from 850°C, whereas the ordered sample had been slowly cooled from 750°C during a period of 100 hours. Extra diffractive features are to be noted at the superstructure line positions (100), (111), and (210) for the ordered sample in contrast to their absence for the disordered sample. Thus, ordering of the type shown in Fig. 1 is indicated for the slowly cooled sample.

The relative intensities of the (100) and (110) reflections of the ordered sample are about 1:5 by experiment and this compares not unfavorably with the calculated ratio 1:6 as shown in Table II. No great accuracy was sought for in the intensity evaluations but the data as such would indicate a fairly high degree of ordering in the sample. Accurate intensity measurements would, of course, permit a calculation of the degree of ordering. A second point of interest in the patterns is the presence of disorder scattering which is discernible in the pattern differences. The diffuse scattering for the disordered sample is about 20 percent larger than that for the ordered sample. A calculation of the disorder scattering (which would be isotropic if complete disorder existed) to be expected for this system gives as the diffuse scattering intensity about 0.6 neutron per minute, whereas the measured value is about 0.8 neutron per minute.

The system Ni-Mn is an interesting one because the superstructure intensities are enhanced as a result of the reversed phase of scattering for manganese with reference to that for nickel. The usual algebraic difference in the superstructure structure factors becomes a numerical sum in this case and the superstructure line intensities become comparable to the ordinary line intensities and can even exceed them in cases of favorable atomic ratio.

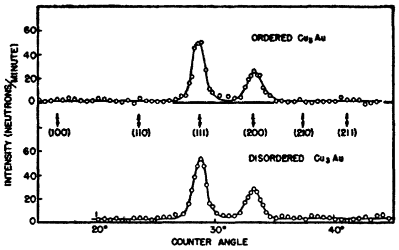

FIG. 4. Neutron diffraction patterns for ordered and disordered samples of Cu_3Au.

Figure 3 shows the patterns obtained for ordered and disordered samples of Ni_3Mn. Extra diffraction features are obtained at the superstructure line positions corresponding to (100), (110), (210), and (211) reflections for the ordered sample. The intensities of the extra lines turn out to be about 50 percent of those expected on the basis of the nuclear scattering amplitudes and this indicates that this particular sample was about 50 percent ordered and 50 percent disordered. The ordered preparation was given a slow cooling for 100 hours from 550°C. The ordered structure corresponds to a face-centered cubic lattice with Mn atoms at the corners and Ni atoms at the face-centered positions.

It has been mentioned earlier that different isotopes of an element can possess different neutron scattering amplitudes. The two major nickel isotopes illustrate this, as shown in Table I, with the Ni^{58} scattering amplitude being nearly five times that for Ni^{60}. This suggests that certain alloy systems can be best studied by selectively using one or the other (or a combination) of particular isotopes. The alloy $MnNi^{60}$ would show, for instance, very unusual patterns: the regular diffraction lines could be made vanishingly weak in comparison to the superstructure line intensities. Ni^{60} would be most suitable for study of the Ni-Fe system whereas Ni^{58} or normal Ni would be preferred in studying Ni-Co combinations.

Patterns for ordered and disordered samples of Cu_3Au are shown in Fig. 4 and here it is to be seen that the superstructure effects are undetectable. This is not unexpected since the neutron scattering amplitudes for Cu and Au are so close in value as listed in Table I. When the patterns of Fig. 4 were obtained, the Au amplitude was unknown and hence these patterns yielded the first value for this amplitude. Subsequent examination of the neutron diffraction pattern for metallic gold confirmed this value. In contrast to the results of the neutron diffraction examination, x-ray diffraction patterns for the ordered and disordered samples, kindly taken for us by Dr. M. A. Bredig, showed pronounced intensity differences indicative of ordering.

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