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SEMI-ANNUAL PROGRESS REPORT ON THE APPLICATION OF DIFFUSE X-RAY SCATTERING TO THE STUDY OF THE STRUCTURE OF BINARY ALLOYS

September 1, 1965 - February 28, 1966

NASA Grant NGR-43-001-018

Submitted to

National Aeronautics and Space Administration

Washington, D. C., 20546

Submitted By

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I. INTRODUCTION

The research in progress under this grant (NASA Grant NGR-43-001-018) consists of an experimental and theoretical investigation of the relationship between the local atomic arrangements in metallic solid solutions and the physical, mechanical, and thermodynamic properties of the solid solutions. During the first six to eight months of the grant most of the research effort was expended toward the growth of satisfactory alloy single crystal specimens for x-ray diffuse scattering measurements of the local atomic arrangements and the development of the necessary experimental apparatus for both x-ray and electrical resistivity measurements. Most of this effort was discussed in the first progress report covering the period March 1, 1965 - August 31, 1965.

The present progress report covers the research effort during the second six-months period of the grant. During this period the bulk of the necessary work on the experimental equipment has been completed and some experimental measurements have been made.

II. PRESENT STATUS OF EXPERIMENTAL EQUIPMENT

It was pointed out in our previous report (1) that the establishment of a facility for measuring the diffuse x-ray scattering from Fe-Al alloys was necessary. This facility, con-

consisting of a source of CoKα radiation monochromated by a germanium single crystal together with an x-ray diffractometer equipped with an Eulerian cradle and cryostat for cooling the sample to liquid nitrogen temperature, has been completed and diffuse scattering measurements begun. The details of the completed apparatus are essentially as described in our previous report (1).

It was also pointed out that we believe that many of the crystal growth problems encountered in our research can be circumvented by using a noble metal wound resistance furnace capable of operation up to 1750°C in conjunction with a mechanism for moving this furnace vertically as in the standard Bridgman technique. A Pt-Rd wound furnace has been purchased (using primarily University funds), and a mechanism for gradually raising it has been constructed. This system is equipped with a high vacuum system and a standard proportioning type temperature controller. A photograph of this system is presented in Figure 1. This equipment is presently being used in an effort to grow some Ni-Pd alloy single crystals.

III. DISCUSSION OF SOME RESULTS

A. The Fe-Al System

The first usable data to be obtained from the recently completed diffuse scattering diffractometer for iron-base alloys is shown in Figure 2. The data presented are the raw intensity measurements of the diffuse scattering on the h_1h_20 plane of reciprocal space from an Fe-14.5 at. % Al crystal. These

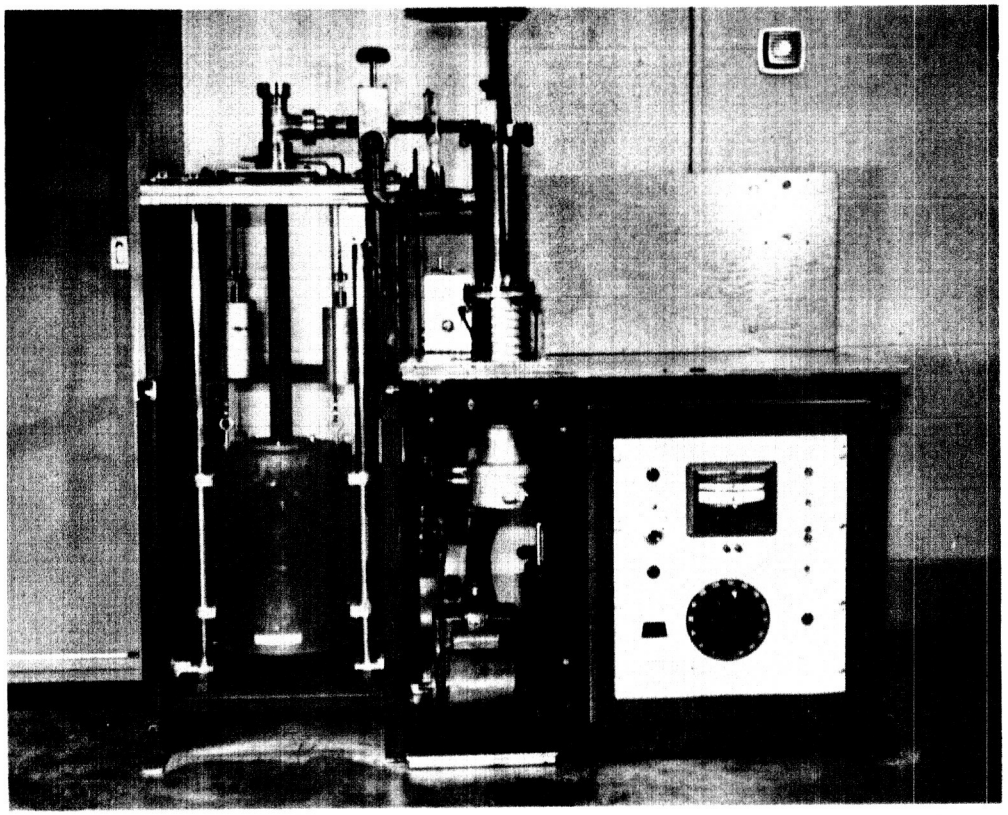

Figure 1. Bridgman furnace for growing single crystals

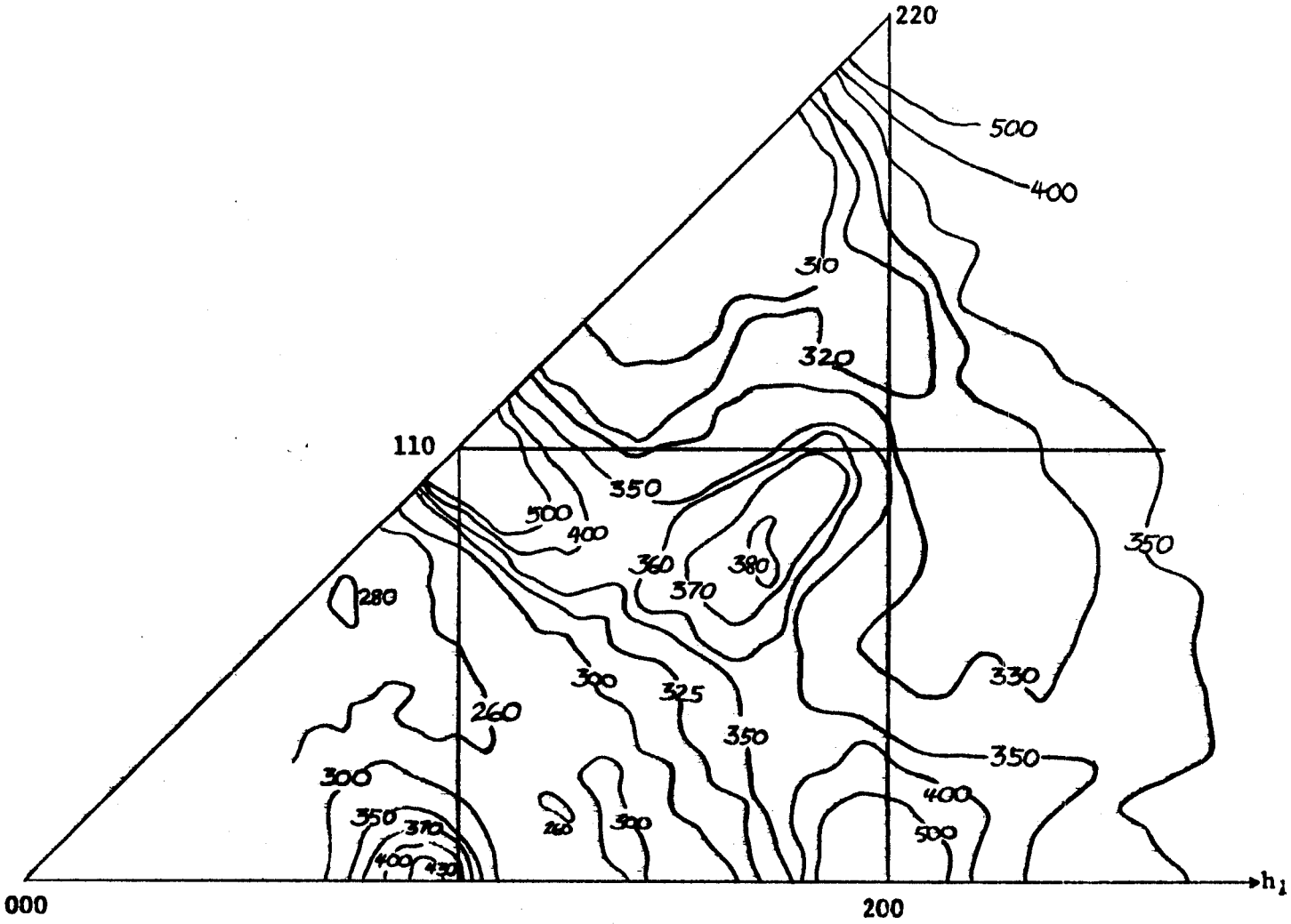

Figure 2. Diffuse intensity distribution on the h_1h_20 plane of reciprocal space for an Fe-14.5 at. % Al sample in arbitrary units. Contours greater than 500 near Bragg reflections are omitted.

intensity data have not been converted to absolute units or corrected for Compton and temperature diffuse scattering. The measurements were made at room temperature on a crystal which had been homogenized in argon for two weeks at 1000°C and then cooled 100°C per day to room temperature.

Although the formal analysis of these data has not been carried through, some important conclusions can be drawn from Figure 2. The diffuse scattering maxima which occur near h_1, h_2 = ½,0 and h_1,h_2 = 1,½ appear to be more consistent with the atomic arrangement in long range ordered FeAl (CsCl-B2 type structure) than with the atomic arrangement in Fe_3Al (BiF_3-DO_3 or $LaMg_3$-B32 type). This may be seen by reference to Figure 3 where the positions of the superstructure reflections in long range ordered FeAl and Fe_3Al are plotted in the h_1h_20 plane of reciprocal space. It is observed that if a tendency to retain the Fe_3Al structure existed in our alloy, then we should observe diffuse maxima near positions such as h_1,h_2 = ¼, ¼ ; h_1, h_2 = ¾, ¾. No such maxima are apparent in the data of Figure 2. This conclusion is contrary to the conclusion of Houska and Averbach, based on powder data, that the Fe-Al alloys containing less than 20 at. % Al have atomic arrangements which are more consistent with the arrangement in long range ordered Fe_3Al (2).

Another obvious feature of the data presented in Figure 2 is that the diffuse maxima do not occur precisely at the expected positions. This fact is possibly due to a strong atomic size effect modulation. An understanding of this effect must await

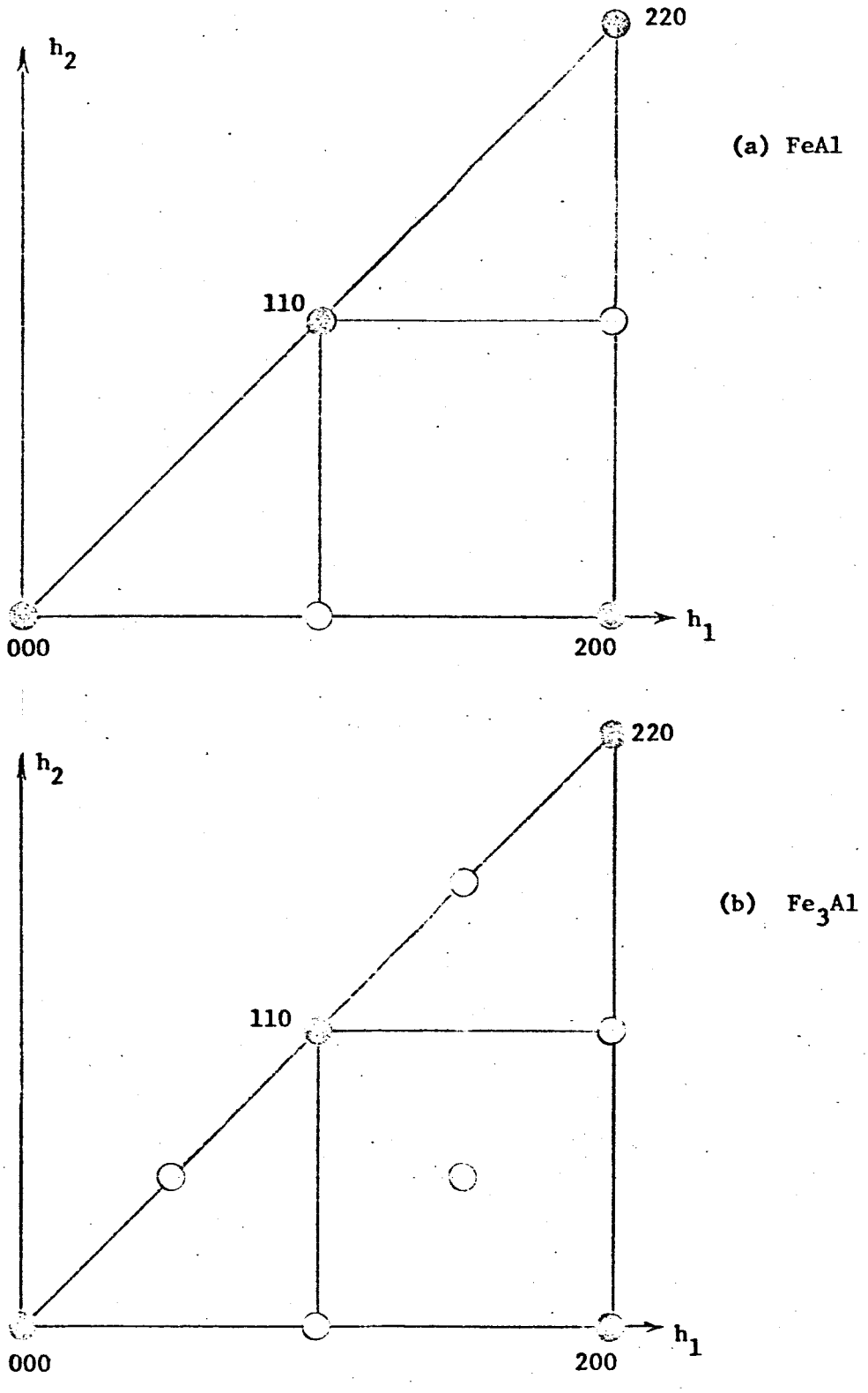

Figure 3. Schematic intensity distribution on the h_1h_20 plane of reciprocal space for long range ordered Fe-Al alloys. Closed circles represent fundamental reflections and open circles represent superstructure reflections.

a more complete set of data and a careful analysis. It would be premature to draw further conclusions from this data at present.

B. Ni-W System

In our first progress report, (1) some x-ray diffuse scattering data taken on the h_1h_20 plane of reciprocal space for a Ni-10 at. % W alloy quenched from 1300° C into iced brine was presented. We have now analyzed this data and obtained two-dimensional short rante order parameters and atomic size effect coefficients. Further data has been obtained and analyzed for this Ni-10 at. % W sample after the following heat treatment: 2 hours at 1000°C, 17 hours at 900°C, 114 hours at 600°C, 36 hours at 800°C, 74 hours at 700°C, 114 hours at 600°C, and 114 hours at 500°C. The two-dimensional short range order parameters for the quenched condition and for the heat treated condition are presented in Table I. These parameters are related to the usual three-dimensional short range order parameters, $\alpha_{\ell mn}$ through the equations

$$A_{\ell m} = \sum_n \alpha_{\ell mn} \quad . \tag{1}$$

Two-dimensional atomic size effect coefficients for samples in the quenched and heat treated conditions are presented in Table II. These coefficients are also defined in terms of the three-dimensional atomic size effect coefficients of Warren, Averbach, and Roberts (3) by

$$B_{\ell m} = \sum_n \beta_{\ell mn} \quad . \tag{2}$$

TABLE I

TWO-DIMENSIONAL SHORT-RANGE ORDER PARAMETERS FOR A Ni-10 At. % W ALLOY

lm	Quenched	Heat Treated*
00	1.062	1.131
10	-0.178	-0.235
11	-0.013	-0.030
20	0.017	0.012
21	0.057	0.047
22	-0.072	-0.077
30	0.008	0.028
31	-0.023	-0.032
32	0.015	0.031
40	0.003	-0.011
41	-0.019	-0.014
33	-0.002	+0.014
42	-0.004	-0.005
43	-0.025	-0.014
50	-0.017	-0.018
51	0.001	0.007
52	-0.012	-0.002
44	0.000	0.025
53	-0.005	0.008
60	-0.009	0.002
61	-0.004	0.003

*See text for heat treatment.

TABLE II

TWO-DIMENSIONAL ATOMIC SIZE EFFECT COEFFICIENTS FOR A Ni-10 At. % W ALLOY

	Quenched				Heat Treated*		
ℓ	m=1	m=2	m=3	ℓ	m=1	m=2	m=3
0	0.012	0.003	-0.001	0	0.015	0.002	-0.002
1	0.005	0.000	-0.001	1	0.005	-0.001	-0.001
2	0.002	0.003	0.000	2	0.001	0.003	-0.002
3	0.001	0.001	0.001	3	0.001	0.001	0.000

*See text for heat treatment.

The values of $A_{\ell m}$ presented in Table I, as well as the intensity data itself, indicate that the heat treatment described above increased the degree of order in the Ni-10 at. % alloy relative to that which existed after quenching from 1300°C. Data taken after the 114 hours at 600°C treatment and prior to the final 114 hours at 500°C indicated, however, that little increase in order takes place with treatments at 600°C or above.

We have obtained three-dimensional short-range order parameters from the two-dimensional parameters presented in Table I for the heat treated sample. These parameters were calculated from equations (1) with the assumption that the α's become negligibly small for coordination shells beyond α_{330}. With this assumption the number of unknowns becomes one less than the number of equations and it is possible to solve for the $\alpha_{\ell mn}$. The results of this calculation are presented in Table III. Since one extra equation (involving parameters with odd indices) is available, it is possible to use it as a check on the value of one parameter, chosen in this case to be α_{110}. The extra equation gave a value of $\alpha_{110} = -0.055$ in good agreement with the value given in Table III. It should be pointed out that the parameters with even indices could not be checked at all, and, furthermore, the value of A_{oo} is used in their determination. Since the value of A_{oo} is dependent on the accuracy of the correction of the intensity data for extraneous effects, the parameters with even indices must be considered to be less

TABLE III

THREE-DIMENSIONAL SHORT-RANGE ORDER PARAMETERS FOR A Ni-10 At. % W ALLOY*

ℓmn	$\alpha_{\ell mn}$
000	1.000
110	-0.061
200	0.076
211	0.008
220	-0.032
310	-0.063
222	-0.022
321	0.015
400	-0.011
411	0.007
330	0.014

*Heat treated condition.

accurate than those with odd indices. The parameters given in Table III are consistent with a model of the short-range structure of the alloys in which the W atoms tend to occupy the same atomic positions that they occupy in a fully long-range ordered alloy of composition Ni_4W.

The atomic size effect coefficients of Table II are approximately the same for the two conditions and are small for both cases. The coefficients are all sensibly positive indicating that the distance between pairs of tungsten atoms in solution is greater than the average distance that would be computed from the lattice constant.

In Figure 4 is presented the electrical resistivity of a Ni-10 at. % W alloy as a function of cold work following annealing at 950°C. These data show that the electrical resistivity decreases with increasing cold work. This unusual behavior is by definition typical of the behavior associated with the so-called "K-state." A similar effect has been found and recently published by Baer (4) in other Ni-W and Ni-Mo alloys in the Ni-rich terminal solid solution range. Baer has attributed the occurrence of the K-state to the existence of short-range order in these alloys. Presumably an increasing degree of short-range order increases the electrical resistivity in Ni-W alloys. Cold working a short-range ordered alloy disorders it and therefore reduces the electrical resistivity. The decrease in resistivity due to the disordering process apparently overrides the usual resistivity increase caused by cold working. We agree that

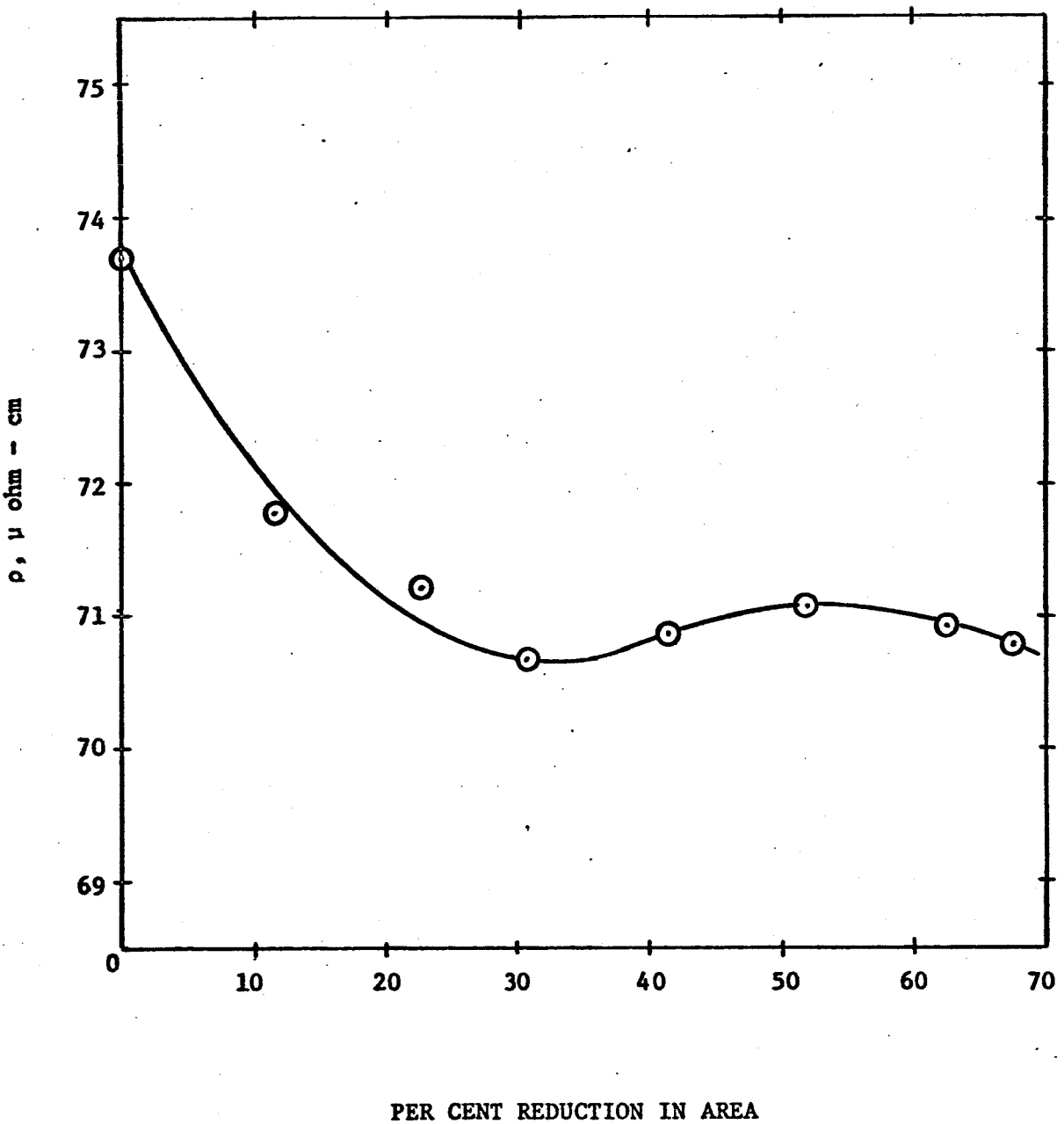

Figure 4. The effect of cold work on the electrical resistivity of a Ni - 10 at. % W alloy previously annealed at 950°C. Measurements made at 72°F.

We agree that short-range order is probably responsible for the observed effects which are associated with the K-state. However, some other questions need to be answered before this problem can be considered settled. For example, why does short-range order cause an increase in the electrical resistivity of some alloys and a decrease for others (5)? And how is a change in the degree of short-range order reflected quantitatively in a change in the electrical resistivity and other properties of the alloy?

Baer points out (4) that single crystal measurements such as those that we are presently performing are needed for a full and unequivocal interpretation of the short-range structure and its relation to the K-state. This need is quite evident when some of Baer's conclusions, drawn from his fairly crude powder measurements, are examined in the light of our single crystal measurements.

Baer concludes that the local atomic arrangements in Ni-W solid solutions are not the same or similar to the atomic arrangements in long range ordered Ni_4W nor do the locally ordered regions act as nuclei for the formation of the long range ordered structure. His conclusion was based on the fact that the local-order intensity peaks do not occur at the same positions as the superstructure reflections for the long range ordered phase. Our single crystal data on Ni-Mo (6) and Ni-W alloys also show that the local-order intensity maxima do not

occur at the same positions in reciprocal space as the intensity peaks for the superstructure. Yet our data are best interpreted in terms of a model for the short-range structure that does indeed indicate a similarity to the structure of long range ordered Ni_4Mo. The precise location of the diffuse intensity maxima are more sensitive to the higher order structure parameters -- a fact which suggests that in Ni-W and Ni-Mo alloys it is the size of the locally ordered regions that accounts for the position fo the diffuse maxima and not that the arrangement of the near neighbor atoms of the locally ordered α phase is so dissimilar from the long range ordered structure.

Because Baer has completed a relatively thorough study of the effects of heat treatment and cold work on the electrical resistivity of Ni-rich Ni-W solid solutions, we believe that we can now do fewer electrical resistivity measurements on these alloys than we had originally planned. Rather than do many more resistivity measurements we believe that more information concerning the nature of these K-state alloys can be gained from measurements of the stored energy as a function of cold work and initial heat treatment and measurements of the specific heat as a function of temperature. We have prepared samples for both types of measurements.

Diffuse scattering measurements will be obtained from polycrystalline samples as a function of cold work in order to correlate the short-range order parameters with the stored

energy measurements. The specific heat measurements will be used to check for the presence of anomalies in specific heat such as have been attributed to the dispersion of short-range order in other alloys (7).

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