An X-Ray Test of Superstructure in $FeNi_3$

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A search has been made for superstructure in permalloy of composition near $FeNi_3$. Curves of x-ray scattering power near the absorption edges of Ni and Fe show that Fe $K\beta$-radiation should give the strongest superstructure lines, and calculations indicate that reflection from (321) planes of a perfectly ordered structure should have about one-seventh the intensity of the ordinary (222) reflection. The specimen was a powdered alloy containing 70 percent nickel, annealed at 1000°C and baked at 425°C. It was placed in a focusing camera in a beam of Fe $K\beta$-rays which were selected and concentrated by a curved rocksalt crystal, and exposed for one hundred hours. No superstructure lines appeared, although superstructure in β-brass was easily detected with similar technique. This negative result, which is supported by a considerable amount of indirect evidence, indicates that no long range order exists in $FeNi_3$.

INTRODUCTION

IN the iron-nickel series of solid solutions the region from 65 to 81 percent nickel has been of outstanding interest because of the extremely high permeabilities developed by suitable heat treatments. The composition at 78.5 percent nickel has long been the standard permalloy, and the highest permeability ever reported[1] (1,330,000) was in a single crystal of permalloy of 65 percent nickel content, the same composition yielding the highest permeability for polycrystalline material.[2] Since this region includes the composition at 75 atomic percent nickel, it has been suggested for many years that the properties might be affected by the formation of a superstructure at $FeNi_3$. Such a structure is very difficult to detect by means of x-ray diffraction because iron and nickel have nearly equal scattering powers. Jette and Foote[3] looked for it in alloys of 79.4 and 66.8 percent nickel, but found no indication of superstructure lines.

However, considerable indirect evidence has appeared which strongly indicates such a superstructure. Dahl[4] has studied the effect of plastically deforming some iron-nickel alloys and found that at 35 and 100 percent nickel changes in resistivity produced by cold working an annealed specimen amounted to only one or two percent, while in the region between these compositions the effect was greater, reaching a maximum of some 34 percent at 75 atomic percent nickel. In this same region quenching also produced resistivities considerably higher than those of the annealed specimens. This is similar to the behavior of some alloys known to have superstructures, notably Cu_3Au. Two cases of large changes in resistivity with cold work where no superstructure exists are known in tungsten, with 50 percent change, and molybdenum, with 18 percent change, but as pointed out by Nix and Shockley[5] these are rather brittle substances and may not be strictly comparable with the more plastic alloys.

Another strong support for the superstructure theory occurs in the specific heat measurements of Kaya.[6] He found a sharp maximum between 500°C and 600°C in the specific heat of the aged alloy, while for the quenched alloy the maximum was much lower. Additional indications of superstructure in $FeNi_3$ are found in the measurements of the lattice spacings of the Fe–Ni series.[7] It was found that from 45 to 100 percent nickel the lattice spacing departed from the linear relation with composition, the change being a slight decrease with a maximum at about 78 percent nickel.

On the other hand, in the few cases in which magnetic measurements have been made on ordered structures exhibiting ferromagnetism, the change from order to disorder is accompanied

[1] R. M. Bozorth, J. App. Phys. **8**, 575–88 (1937).
[2] Joy F. Dillinger and Richard M. Bozorth, Physics **6**, 279–284 (1935).
[3] Eric R. Jette and Frank Foote, *Metals Technology*, Tech. Pub. No. 670 (1936).
[4] O. Dahl, Zeits. f. Metallkunde **28**, 133–138 (1936).
[5] Foster C. Nix and William Shockley, Rev. Mod. Phys. **10**, 57 (1938).
[6] Seiji Kaya, J. of the Faculty of Science, Series II, Vol. II, No. 2, Hokkaido Imperial University, Sapporo, Japan.
[7] A. J. Bradley, A. H. Jay, and A. Taylor, Phil. Mag. **23**, 545–557 (1937); E. A. Owen, E. L. Yates, and A. H. Sully, Proc. Phys. Soc. **49**, 318 (1937).

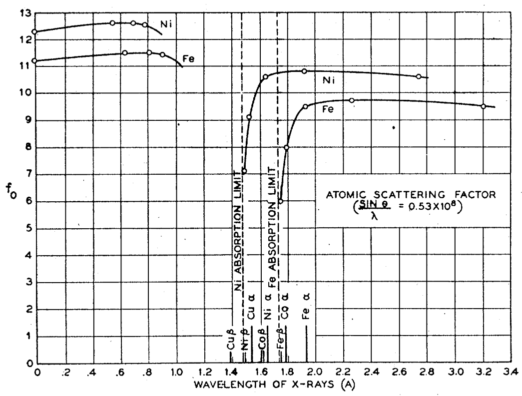

FIG. 1. Atomic scattering factors of Fe and Ni as a function of wave-length. On the wave-length scale are marked the positions of the $K\alpha$- and $K\beta$-rays from Cu, Ni, Co and Fe.

by changes in the saturation magnetization at room temperature and in the Curie point. This is especially true of those which in the disordered state have no ferromagnetism, such as Ni_3Mn and the Heusler alloy Cu_2MnAl. In the 70Ni permalloy no significant change in saturation magnetization has been found on comparing the annealed with the hard worked alloy.

All of these are indications only, not direct proof, and hence it appeared desirable that a more exhaustive test be made. Recent improvements in methods have increased the probability of obtaining x-ray diffraction lines characteristic of superstructures in cases formerly considered out of the question, and the present work was undertaken to apply these methods to $FeNi_3$. This involved choice of the x-rays of the most suitable wave-length, selecting and concentrating them into as intense a beam as possible, and using a focusing camera covering the reflection angle in which lies the strongest superstructure line.

Choice of Radiation

The difference in x-ray scattering powers of two neighboring elements may be increased if advantage is taken of the fact that near the absorption edge of an element its scattering power is greatly decreased. This was used by Mark and Szillard[8] in a study of KBr, by Bradley and Rodgers[9] in demonstrating superstructure in a Heusler alloy, and recently by Jones and Sykes[10] on β-brass. By using Zn $K\alpha$-radiation the latter were able to increase the difference between the atomic scattering powers of Cu and Zn from about 0.6 to 2.1, thus increasing the intensity of the superstructure lines by a factor of about twelve.

In Fig. 1 is shown the atomic scattering curve of Ni as determined by Jesse,[11] together with a corresponding curve for Fe, derived from it. From this it is seen that the Fe $K\beta$-radiation, which is very close to the iron absorption edge, is scattered with the greatest difference. Recently Bradley and Taylor[12] have reported that they used Co $K\alpha$-radiation in a test for superstructure of $FeNi_3$ and found no indication of any. Co $K\alpha$ gives a reflecting power for the superstructure lines somewhat less than half that for the Fe $K\beta$. Jette and Foote[3] and Kaya[6] both used Ni $K\alpha$-radiation in their studies. This wave-length lies between the absorption limits of iron and nickel and hence is strongly absorbed by iron. Very little is known of the scattering curve on the short wave-length side of the absorption limit because the reflections are weak and the background scattering high. Hence Ni $K\alpha$-radiation is very unsuitable and might even lie close to where the two curves cross, thus giving a difference in scattering power less than that for any other radiation which might be chosen.

Calculations were made of the relative intensities of all possible reflections of Fe $K\beta$-radiation from $FeNi_3$, allowing for absorption in the specimen and the effect of temperature.

TABLE I. *Calculated intensities for* $FeNi_3$.

		Intensity				Intensity	
h k l	θ	Ord. Line	S. S. Line	*h k l*	θ	Ord. Line	S. S. Line
100	14.3		5.4	300, 221	47.7		14.3
110	20.4		8.3	310	51.3		13.3
111	25.3	703		311	54.9	1140	
200	29.6	402		222	58.7	435	
210	33.4		11.2	320	62.8		21.6
211	37.2		10.6	321	67.3		58.7
220	44.3	499		400	80.6	1350	

[8] H. Mark and L. Szillard, Zeits. f. Physik **33**, 688–691 (1925).

[9] A. J. Bradley and J. W. Rodgers, Proc. Roy. Soc. Lond. **A144**, 340 (1934).

[10] F. W. Jones and C. Sykes, Proc. Roy. Soc. Lond. **A161**, 440 (1937).

[11] Williams P. Jesse, Phys. Rev. **52**, 443–451 (1937).

[12] A. J. Bradley and A. Taylor, Proc. Roy. Soc. **166**, 353–375 (1938).

These are given in Table I, and show that the reflection from the (321) planes should be the superstructure line easiest to detect.

Experimental

The apparatus consisted of a Phillips-Metalix x-ray tube with Fe target, a bent curved crystal of rocksalt to select and concentrate the Fe $K\beta$-radiation, and a symmetrical focusing camera. These were arranged as shown in Fig. 2, a more complete description being given in an earlier paper.[13] The specimen was prepared from permalloy containing 70 percent nickel by filing powder from a quarter-inch bar. This was mixed with sufficient quartz dust to prevent sintering and annealed for 1 hour at 1000°C and then for 5 hours at 425°C. The powder was spread on a curved brass strip, and mounted on the circumference of the camera. The angular range covered by the camera was such that the (311), (222), (320), (321) and (400) reflections could be recorded. The film was exposed in this position for 100 hours and then taken out and cut in half. About an inch was cut off the end of one half and then this half was replaced in the camera with its position shifted one inch and re-exposed for about five hours. The two sections of film were then developed and fixed together. The second exposure gave reflections from the (311) and (222) planes of intensities equal to and about one-third of the expected intensity of the (321) superstructure line, on a background of like intensity. No reflections from the (321) planes or the (320) planes could be observed although the five-hour exposure of the (222) reflection, which should have only one-third the intensity of the (321) reflection, is very plainly visible and the five-hour (311) reflection, which should be equal in intensity to the (321) reflection, has considerable intensity. The two halves of this film are reproduced unretouched in Fig. 3.

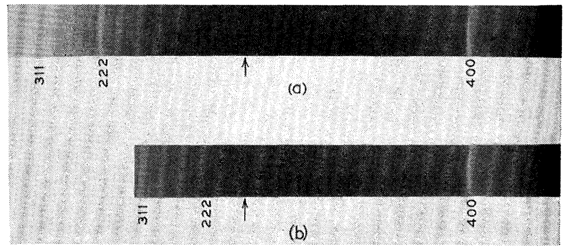

FIG. 3. X-ray diffraction pattern of $FeNi_3$ exposed to Fe $K\beta$-rays for 100 hours. Section (a) is one half as originally exposed; section (b) is the other half after cutting off the end and re-exposing for five hours in a different position, giving the fainter (311) and (222) reflections as shown. The (321) superstructure lines would be at the points indicated by the arrows and should be as intense as the (311) line on section (b) and three times as intense as the (222) line on section (b).

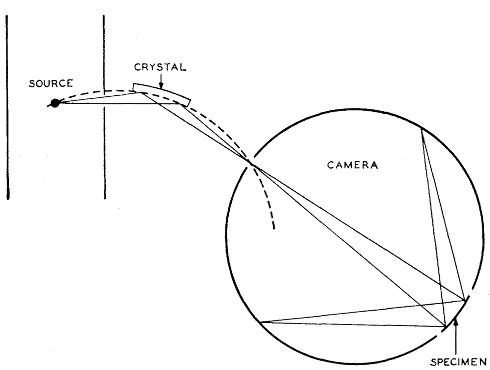

FIG. 2. Arrangement of apparatus. The Fe $K\beta$-rays from the source are brought to a focus by the bent and cut rocksalt crystal at the camera circumference. They then diverge to the specimen and after reflection are refocused at the film.

This film was the culmination of many attempts to detect superstructure lines in $FeNi_3$. In one of these the material was rolled into strips, annealed for one hour at 1000°C, and then for 100 hours at 425°C. This gives the crystallites a preferred orientation, and advantage was taken of this to set it at just the proper angle to give a maximum reflection from the (321) planes. After an exposure of 70 hours no (321) reflection appeared. As a further check of the technique some β-brass was prepared, and given sixteen hours exposure to Cu $K\beta$-radiation by the method first described. The superstructure line from the (320) planes was observed, although by calculation its intensity should be only *one twenty-eighth* that of the expected (321) reflection from the $FeNi_3$. The β-brass was given another exposure of sixty-four hours to have the reflection strong enough for reproduction and this is shown in Fig. 4.

Thus it seems reasonable to conclude from these experiments that no superstructure exists in $FeNi_3$ of sufficiently long range to form an x-ray diffraction pattern.

[13] R. M. Bozorth and F. E. Haworth, Phys. Rev. **33**, 538–544 (1938).

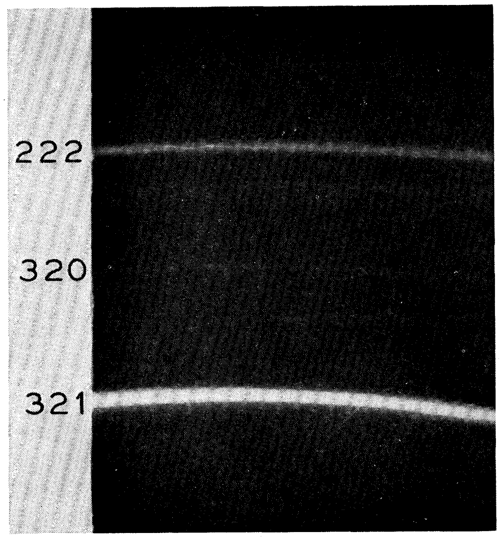

FIG. 4. X-ray diffraction pattern of Cu Zn exposed to Cu $K\beta$-rays for 64 hours. The superstructure line is the one marked (320).

DISCUSSION

There still exists the possibility that there is order in $FeNi_3$ of such a short range that no diffraction lines could be obtained, and no definite statement can be made of whether this would produce the observed change in resistivity. In the Cu_3Au alloy Sykes and Jones[14] found that for all treatments which gave it resistivities such that ordering would be expected, superstructure lines were found, and from this it seems logical that ordering sufficient to produce detectable superstructure lines and ordering sufficient to affect resistivity are concomitant, but there are not sufficient data to establish such a generalization.

Another criterion which may be useful in such problems and which I have not yet seen proposed in the literature is this: It is well known that for materials in which no superstructure exists, Matthiessen's rule is obeyed when the annealed material is cold worked, i.e., the slope of the resistivity *vs.* temperature curve does not change; this is true even for tungsten[15] which changes its resistivity by as much as 50 percent when cold worked; but for all cases of definite superstructures for which resistivity-temperature curves are reported in the literature, Matthiessen's rule is *not* obeyed in changing from the ordered to the disordered state. These data are listed in Table II.

There appear to be no data available on resistivity *vs.* temperature for cases in which superstructure is destroyed by cold work, but Dahl[4] has found that cold working the quenched Cu_3Au alloy changed its resistivity by less than

TABLE II. *Comparison of materials with and without superstructure with respect to Matthiessen's rule.*

Materials	$d\rho/dT$ (ohm cm/deg.) $\times 10^8$			Percent Change	Reference
	Quenched	Cold Worked	Annealed		
With Superstructure					
Cu_3Au	0.68		1.12	+65	16
CuAu	0.64		0.96	+50	17
Cu_3Au	0.74		1.03	+39	18
CuAu	0.90		1.28	+42	18
38% Pd, 62% Cu	0.40		0.59	+47	18
Ni_3Mn	1.2		5.8	+380	19
Without Superstructure					
W		2.60	2.64	+1.5	15
Mo		2.69	2.67	−0.7	15
Ni		5.10	4.97	−2.5	15
Pt		4.13	4.17	+1.0	15
Ni				+0.1	20

[14] C. Sykes and F. W. Jones, Proc. Roy. Soc. **A157**, 213 (1936).
[15] W. Geiss and J. A. M. v. Liempt, Zeits. f. Physik **41**, 867 (1927).
[16] C. Sykes and H. Evans, J. Inst. Metals **58**, 255 (1936).
[17] U. Dehlinger and L. Graf, Zeits. f. Physik **64**, 359 (1930).
[18] G. Borelius, C. H. Johansson and J. O. Linde, Ann. de Physik **86**, 291–318 (1928).
[19] S. Valentiner and G. Becker, Zeits. f. Physik **93**, 795–803 (1935).
[20] Heinz Bittel, Ann. de physique **31**, 219 (1938).

two percent, thus indicating that it is similar in properties to the quenched alloy.

The curves from which the values of $d\rho/dT$ for the ordered state were taken probably do not represent complete order, but for complete order the slope should be greater if any different. This may be shown by a consideration of the Cu_3Au curves, those of Sykes and Evans being reproduced in Fig. 5. On the basis of Peierls[5] application of Bethe's theory to alloys of type AB_3, the value of the critical temperature is,

$$T_c = 1.33E_0/R,$$

where E_0 is the energy of transformation from perfect order to randomness. The temperature at which the equilibrium curve departs appreciably from perfect order is $T = 0.75E_0/R$. Since T_c for Cu_3Au is 654°K (381°C), T will be 368°K or 95°C. Therefore at room temperature any departure from perfect order should be due to failure to attain equilibrium rather than destruction of ordering by thermal agitation. And since we should expect the curve to be nearer equilibrium at the higher temperatures, if the experimental curve (A) of Fig. 5 is not the equilibrium curve, we should expect the latter to look more like (B), than like (C). In other words, if the material is not in equilibrium, the slope of the curve at room temperature should lie *between* that of the completely disordered state and the equilibrium curve. Hence if the changes of slope recorded in Table II are for the conditions for which equilibrium is not attained, the changes are less than the true values and Matthiessen's rule would be violated even further at equilibrium.

Resistivity data on the permalloy specimens used in the present experiments were taken by Dillinger[21] and confirmed Dahl's measurements of the change in resistivity with cold working. At the same time data were taken on $d\rho/dt$, but not published. He found that for the cold rolled specimen $d\rho/dt$ was 9.3×10^{-8} ohm cm/deg. and for the specimen annealed at 460°C it was 8.5×10^{-8}, a *decrease* of about 8.6 percent. Thus it does not obey Matthiessen's rule closely, but the fact that the change is small compared to those in the known superstructures and in the

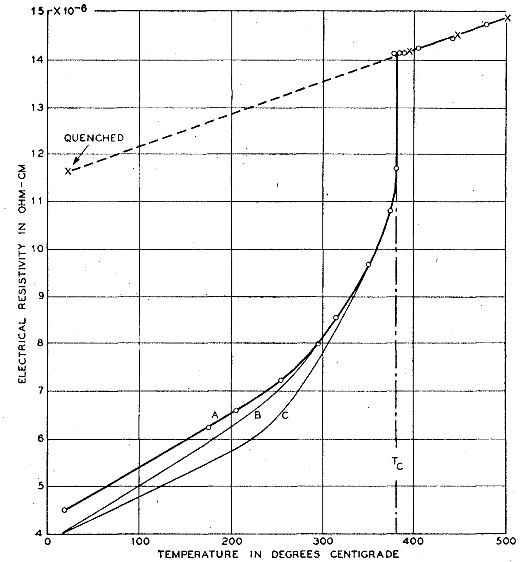

FIG. 5. Electrical resistivity-temperature curve for Cu_3Au. The experimental curve is marked A, and is in equilibrium at temperatures above 350°C.

opposite direction is indicative of the absence of superstructure.

The measurements of Kaya[6] on the specific heat of an alloy containing 24.1 percent iron provide such strong evidence of ordering that they will be considered in some detail. He found that the additional energy under the large maximum of the curve for the aged alloy was 14.57 cal./g while for the quenched alloy it was only 2.09 cal./g. His assumption was that the former represented the energy associated with the disappearance of ordering plus that of the magnetic transformation, while the latter was due to the magnetic transformation only. In accord with this idea was a calculation of the energy of ordering after the theory of Bragg and Williams, from which,

$$Q = RT_c/2.26M = 11.7 \text{ cal./g},$$

in which T_c is taken as 773° (500°C), and M is the atomic weight. But the theory as modified by Peierls for application to structures of the AB_3 type yields instead

$$Q = RT_c/1.33M = 19.0 \text{ cal./g}.$$

Stoner[22] has considered very carefully the energy change due the magnetic transformation in pure nickel as obtained from specific heat measure-

[21] J. F. Dillinger, Phys. Rev. **49**, 862 (1936).

[22] Edmund C. Stoner, Phil. Mag. **22**, 81–106 (1936).

TABLE III. *Properties of* $FeNi_3$ *for which a change by long range order would be expected and the results as known.*

PROPERTY	CHANGE	INDICATION
Resistivity, ρ	Increase on cold working or quenching	Ordering
$d\rho/dT$	-8.5% on annealing the cold worked alloy	No ordering
Magnetic saturation at room temperature	No change	No ordering
Magnetic permeability	High on quenching	None
Specific heat	15 cal./g peak	Ordering or magnetic transformation
X-ray diffraction	No superstructure lines	No long range ordering

ments, and obtains 191 cal./g-atom = 3.3 cal./g. Since from theoretical considerations one would expect the energy to vary directly with the Curie temperature and the saturation magnetization, for $FeNi_3$ the energy should be

$$Q = 3.3(870/630)(12200/6100) = 9.1 \text{ cal./g.}$$

This shows that if long range order is present we should expect the specific heat measurements to give a value of about 28 cal./g, while if it is absent a value of about 9 cal./g. Thus there is reason to expect that Kaya's value for the aged specimen, 15 cal./g, can be explained by the magnetic transformation. In this case the value for the quenched material is too small and is difficult to understand.

Kaya points out also that if there is ordering in $FeNi_3$, the high permeability is associated not with its presence but with its prevention, since the high permeability is produced by rapid cooling or quenching, and is reduced on aging. This effect would be in the direction opposite to the usual result; e.g. in Ni_3Mn the permeability at room temperature is increased by ordering.

The properties of $FeNi_3$ which one would expect to be affected by long range order and the results as known to date are summarized in Table III.

Thus the negative result of the x-ray work indicates definitely that no long range order exists in $FeNi_3$, and this nonexistence is supported by a considerable amount of less direct evidence.

The author wishes to acknowledge his indebtedness to Drs. R. M. Bozorth, F. C. Nix, and W. Shockley for many valuable discussions.

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A Determination of e/m from the Refraction of X-Rays in a Diamond Prism

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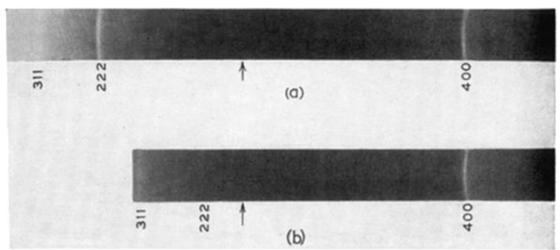
Measurements of the index of refraction of the copper K_β line by a diamond prism have been made with an estimated accuracy of one part in 10,000. These measurements together with the quantum theory of dispersion and the ruled grating wave-length of the copper K_β line afford a method of evaluating e/m with an accuracy comparable to that of previous determinations by other methods. The value of e/m is given by the equation

$$\frac{e}{m} = \delta\left[\frac{\lambda^2\rho F}{2\pi W}\sum_1^s N_s\{1+A\}\right]^{-1},$$

where δ, λ, ρ, R, N_s and W have their usual meaning and A is the factor which takes into account the electronic binding. For carbon and a $\lambda^{2.75}$ law of absorption, the value of the $\sum_1^s = 6.0163 \pm 0.0006$. Using $\delta = 9224.4 \times 10^{-9}$, $W = 12.0148$, $\rho = 3.5154$, $F = 96513.1$, $\lambda = 1.39220\text{A}$, one obtains $e/m = (1.7601 \pm 0.0003) \times 10^7$ e.m.u. This bound electron value is higher than most previous spectroscopic determinations but is in excellent agreement with the free electron results of Dunnington.

IN the present unsettled state of the values of the fundamental constants it is of importance to determine the value of each constant by as many different methods as possible. In practically all of the experimental methods of evaluating constants, in reality one only measures the value of the constant of proportionality in an equation connecting a group of constants. Precise measurements of the refractive index for x-rays in material of low atomic number together with the dispersion theory afford such a method of evaluating either the wave-length of the x-rays used or the constant e/m. The other constants entering the equation are either known or can



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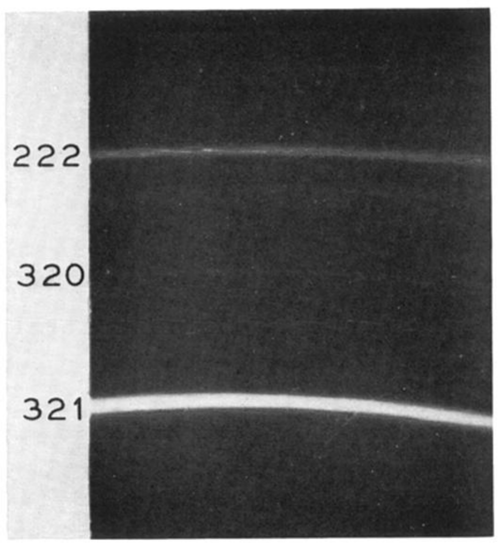

FIG. 4. X-ray diffraction pattern of Cu Zn exposed to Cu $K\beta$-rays for 64 hours. The superstructure line is the one marked (320).