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The Atomic Vibrations of a Zn-Cu Alloy

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Measurements of x-ray reflection intensities at two temperatures have been made on the $21\bar{3}1$ and $10\bar{1}5$ lines from an alloy of copper and zinc. The idea is put forward that the atomic vibrations should be greatest along the c axis of the crystal in case the axial ratio is greater than 1.633, least when the axial ratio is less than 1.633. The values obtained for the relative amplitudes of vibration along and perpendicular to the c axis confirm this idea. The relative atomic structure factors are also found and show a surprising dependence on the angle which the normal to the reflecting plane makes with the c axis.

1. INTRODUCTION

SEVERAL workers[1] have shown that the atomic vibrations in zinc crystals are anisotropic. Brindley's[2] work on cadmium crystals indicates that its atomic vibrations are also anisotropic. Now zinc and cadmium both crystallize in the so-called "hexagonal close-packed system," and have axial ratios of 1.86 and 1.89 respectively, whereas a system of close-packed geometrical spheres would have an axial ratio of 1.633, so that Zn and Cd both have an abnormal separation of the atoms along the direction of the c axis of the crystal. The interesting thing is that the atomic vibrations are greatest along the direction in which the atoms are furthest apart. Brindley and Ridley,[3] in fact, believe that the asymmetry of these crystals is due wholly or in part to these asymmetric atomic vibrations. However, it has been repeatedly observed in this laboratory that the axial ratio changes by only a very small amount when the crystals are cooled to the temperature of liquid air, at which temperature the atomic vibrations are only about $\frac{1}{2}$ as large as they are at room temperature, so that the atomic vibrations may be said to have very little to do with the anisotropy of the crystal. It would seem that the asymmetry of the atomic vibrations is an effect rather than the cause of the lattice asymmetry.

We may picture (rather crudely) the potential function along a given direction, such as the c axis, which would exist if the atom under consideration were removed from the crystal without altering the position of any of the other atoms, as being a U shaped curve (see Fig. 1*a*) with the bottom of the U at the normal rest position of the atom that has been removed. The last requirement is necessary in order that the crystal be stable. If now, the crystal is stretched out in the direction of the c axis, as it is in Zn and Cd, the whole curve would be stretched horizontally (see Fig. 1*b*), the bottom of the U would become more nearly flat and for a given thermal energy the atom would execute larger vibrations than before. In the case of close-packed geometrical spheres (axial ratio $c/a=1.633$) the distance from any atom to each of its nearest neighbors is the same, and thus one would expect the atomic vibrations to be the same in all directions. According to Brindley[4] this seems to be very nearly true for Mg ($c/a=1.624$).

The purpose of the present research was to see if this idea could be extended to crystals having an axial ratio less than 1.633. The elements beryllium, titanium, zirconium, hafnium, yttrium, ruthenium, and osmium have axial ratios between 1.58 and 1.59. In addition, certain alloys have low axial ratios, and in particular the alloy of Zn and Cu which contains 15 atomic percent of Cu has an axial ratio[5] of 1.556. This alloy has the advantage that it differs only slightly from pure Zn since the 15 percent of Zn atoms (atomic No. 30) are replaced

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[1] G. W. Brindley, Phil. Mag. **21**, 790 (1936); G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 408 (1936); E. O. Wollan and G. G. Harvey, Phys. Rev. **51**, 1054 (1937).

[2] G. W. Brindley, Proc. Leeds Phil. Soc. **3**, 200 (1936).

[3] G. W. Brindley and P. Ridley, Nature **140**, 461 (1936).

[4] G. W. Brindley, Nature **138**, 290 (1936).

[5] E. A. Owen and L. Pickup, Proc. Roy. Soc. **140**, 179 (1933).

by Cu atoms of atomic No. 29. Thus we have a crystal which is essentially a zinc crystal compressed along the c axis, and if our hypothesis is correct, the atomic vibrations should be greatest in a direction normal to the c axis.

For an isotropic crystal (in which case the amplitudes of atomic vibrations are equal in all directions) one gets a smooth curve when the atomic structure factors, f_T, are plotted against $(\sin\theta)/\lambda$, where θ is the Bragg angle for radiation of wave-length λ. Since the f_T are proportional to the square roots of the reflection intensities, and since the reflection intensities decrease as the amplitudes of atomic vibration normal to the reflecting plane increase, it appears possible to detect the relative amplitudes of vibration along and perpendicular to the c axis of the crystal by finding the f_T values. Thus, if our hypothesis is correct, we should expect the f_T values for reflections from planes making a small angle with the c axis to give lower values than those from planes making a large angle with the c axis. It will be seen in Fig. 2 that this is true, and hence the question of the relative amplitudes of atomic vibration might seem to have been answered. The theory of the temperature effect on reflection intensities (see Eqs. (1), (3.0), (6)) shows, however, that the temperature effect should decrease with $(\sin\theta)/\lambda$. It will be noticed in Fig. 2 that just the reverse is true. This means that another effect is coming into play. What this effect is will be left for later discussion, but in any event f_T values do not prove conclusively whether an asymmetry in the atomic vibrations exists or not.

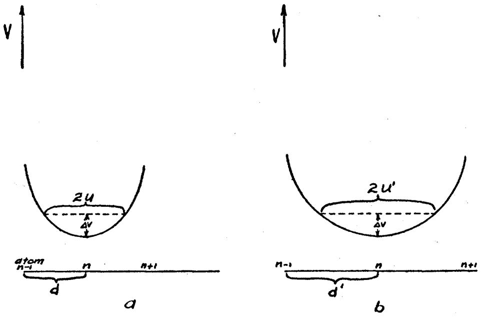

FIG. 1. V is the potential of the nth atom along a given line of atoms in a crystal. ΔV represents the thermal energy of the atom due to vibrations along this line, and u, u' the amplitudes of vibration. d and d' are the distances between atoms for crystals a and b, respectively.

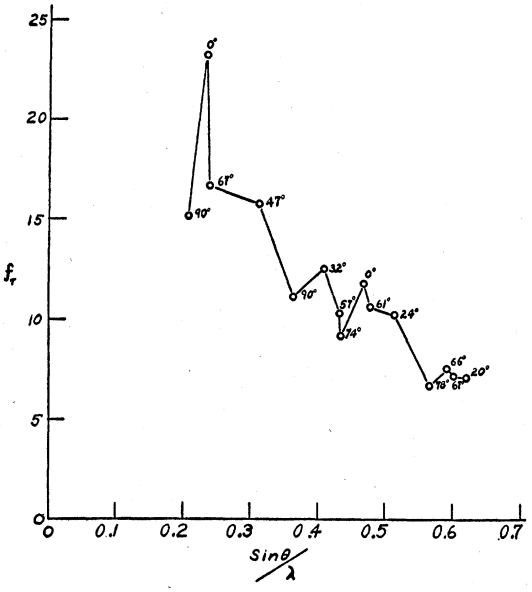

FIG. 2. Atomic structure factor of Zn 85 percent, Cu 15 percent (atomic percent) *vs.* $(\sin\theta)/\lambda$.

Since the f_T values gave inconclusive evidence of atomic vibration asymmetry, it was decided to try the method used by Wollan and Harvey[1] to find the vibration asymmetry in zinc. This method consists in comparing the reflection intensities at two different temperatures. If it is assumed that whatever other causes may make the reflection intensities greater or smaller, their temperature dependence still follows the theories of Debye-Waller, and Zener, then it is possible to determine the quantities a_T and b_T in Eq. (6.0). Since a_T and b_T are proportional to the mean squares of the atomic vibrations along and perpendicular to the c axis, respectively, it is possible to test the atomic vibration asymmetry hypothesis independent of other effects.

2. DESCRIPTION OF APPARATUS

In determining the atomic structure factors, a metal, self-rectifying, x-ray tube designed by Dr. E. O. Wollan and the author was used in conjunction with a zinc crystal monochromator. Cu $K\alpha$ rays were selected and allowed to fall on the powdered alloy at the center of a circular camera of radius 4.5 cm. The total length of the path of the x-rays from target to film was about 14 cm. With this arrangement it was possible to get good photographs in from three to five hours, and the use of a crystal monochromator has the advantage that there is almost no divergence of the incident x-rays and hence no focusing, which means that the lines are all of comparable width. This makes it possible to microphotometer all the lines on one film instead of having to microphotometer different sets of Debye-Scherrer lines on different films and then match the overlapped portions. The monochromatic rays from a crystal also give much less background fogging on the film, and the background is far more uniform than it is when filtered radiation is used. This latter fact makes it possible to determine the background with considerably more precision than is possible when filtered radiation is used.

The apparatus used for the temperature effect work has been described in a paper by Wollan and Harvey.[1] In this case two nickel filters were used to get the Cu $K\alpha$ rays. It was found advisable in all cases to clean the surface of the target frequently as this improves the relative amount of characteristic radiation given out by the tube. The background on the film is reduced and the exposure time is shortened. The x-ray outfit was supplied with current from a "constant voltage generator" and the high voltage and emission current were manually adjusted to a set value every five minutes during the exposure in order to get constant radiation output. In half of the cases, the low temperature exposure was made first so that any diminution in x-ray intensity due to progressive coating of the target would average out when several films were used. The microphotometer used in measuring the line intensities on all films consisted of a caesium cell and a DuBridge balanced-bridge d.c. amplifier to operate a short period Moll galvanometer, together with a mechanical system for scanning the film and moving the sensitized paper by proportionate amounts.

3. Experimental Procedure

The alloy was prepared by mixing powdered pure Cu and Zn in proper proportions to give an alloy containing fifteen atomic percent of Cu. The mixed filings were sealed in a quartz tube and heated to 600°C for a period of eleven hours, and then quenched from the molten state in cold water. This gives an alloy in the ϵ phase of the Zn-Cu system with a melting point of 500°C.[6] After quenching, the alloy was annealed for twenty-four hours, gradually heated to 400°C, slowly cooled to 200°C, and then allowed to cool in air. Filings made by a fine file were sealed in an evacuated Pyrex tube and annealed for thirteen hours at 300°C. The Debye-Scherrer lines obtained with this powder had too many spots on them for intensity measurements, so the filings were ground in an agate mortar with a small amount of powdered KCl. After one and a quarter hours of grinding the KCl was dissolved away with water and the alloy powder dried but not reannealed. The average particle size was about 2×10^{-3} cm after grinding, which is only slightly smaller than before grinding. The chief function of the grinding seemed to be to cold-work the metal particles, as the spots on the Debye-Scherrer lines were now small enough that they did not interfere with intensity measurements. Owen and Pickup[5] give the value 1.556 as the axial ratio of this alloy. By plotting the experimentally determined values of $(\lambda/\sin\theta)$ for the alloy used here on Hull and Davey's[7] logarithmic scale and then using their chart, it was confirmed that the crystal belonged to the hexagonal close-packed system and had an axial ratio of 1.56 as nearly as it could be determined.

In finding the atomic structure factors, several Debye-Scherrer photographs were made. Each film had a set of intensity steps made on it so that any difference in the film or its development would not affect the determination of the relative intensities of the lines. The intensity steps were made by placing the film, held in a lead cassette with a rectangular aluminum window at one end, behind a rotating, step-cut wheel and allowing nickel filtered x-rays from a copper target to fall on it. The wheel was so cut that each successive strip on the film received the same increment of radiation energy. The relative intensities were measured by microphotometering the films and measuring the areas under the curves obtained for the various lines. After the intensities had been corrected for absorption in

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[6] *International Critical Tables*, Vol. 2, p. 435.

[7] A. W. Hull and W. P. Davey, Phys. Rev. **17**, 549 (1921).

the briquet from Brindley's[8] curve, the values obtained were multiplied by a suitable constant so that the corrected relative intensities from each film were on the same basis. The relative atomic structure factors, f_T, were then calculated from the formula

$$I/A = \text{const.} \times pS^2 f_T^2 \phi(\theta), \qquad (1)$$

where p is the multiplicity factor, S the crystal structure factor ($=1$, 2 or $(3)^{\frac{1}{2}}$ for hexagonal close-packed lattices), and

$$\phi(\theta) = \frac{1+\cos^2 2\beta \cos^2 2\theta}{\sin \theta \sin 2\theta}, \qquad (2)$$

where θ is the Bragg angle for the reflection and β is the angle which the incident radiation makes with the monochromator crystal face. In this case $\cos^2 2\beta = 0.649$.

In the temperature effect work, two exposures were made on the same film, one at room temperature and one at the temperature of liquid air. Intensity marks were made on each film as before. Nothing was changed between the two exposures except the position of the film. The angle θ changes so little because of lattice contraction, that changes in the absorption factor, A, may be neglected. Only the $21\bar{3}1$ and $10\bar{1}5$ lines were used in this part of the work. The ratio of the intensity at liquid-air temperature to that at room temperature was determined for each line, in some cases by measuring the areas under the microphotometer traces, sometimes by comparing the heights of the two curves, and occasionally by both methods. The sums of the ratios obtained by the area method and the height method were 23.52 and 23.04, respectively, for the sixteen cases where measurements were made by both methods. Each line was microphotometered from one to nine times and the average value used. The mean values of the ratios for these two lines were then substituted in the Debye-Waller and Zener formulas (Eqs. (3.0) and (4)) and the values of a_T and b_T calculated.

4. RESULTS

Table I shows the relative atomic structure factors obtained, and Fig. 2 is a plot of these values against $(\sin \theta)/\lambda$.

Debye has shown that for a given reflection,

$$I_T = I_0 e^{-2M_T}, \qquad (3.0)$$

where I_T is the intensity of the reflection, I_0 is the intensity which one would get if the crystal were at the absolute zero of temperature, and M_T is a function of the temperature. Let I_{LA} = intensity

TABLE I. *Atomic structure factors.*

LINE	SIN θ/λ	Ψ	RELATIVE INTENSITIES CORRECTED FOR ABSORPTION (I/A)									$pS^2\phi(\theta)$	f_T	f_0
			A-19	A-29	A-39	A-40	A-41	A-46	A-48	A-49	A-50			
$10\bar{1}0$	0.207	90°		9.10	8.50							43.9	15.2 ±1.73	16.5
0002	.234	0°	21.0	22.6	19.5							44.9	23.2 ±0.32	25.2
$10\bar{1}1$	.238	60° 55′	46.7		47.0							194.	16.8 ±0.16	18.6
$10\bar{1}2$	.312	41° 55′	6.12	6.08	6.62			7.00		8.74	10.6	35.1	15.7 ±0.50	18.5
$11\bar{2}0$	.363	90°	5.73	4.84	5.73	5.00		5.36	5.73	5.53	5.90	50.7	11.2 ±0.10	14.3
$10\bar{1}3$	.408	31° 41′	8.68	8.56	7.83	7.51		10.2	7.98	7.30	7.97	59.7	12.6 ±0.16	16.7
$20\bar{2}0$	.417	90°									1.44(?)	9.66		
$11\bar{2}2$	.432	57° 19′			8.01			7.18	6.93	6.06	6.11	73.4	10.3 ±0.18	14.3
$20\bar{2}1$	.434	74° 31′			3.98			4.08	3.56	4.22	4.40	54.7	9.23±0.11	13.1
0004	.468	0°			1.47			1.22	1.40	1.37	1.26	11.2	11.8 ±0.14	16.5
$20\bar{2}2$	.478	60° 55′			1.45				1.62	1.76	1.70	16.4	10.6 ±0.16	16.0
$10\bar{1}4$	.512	24° 5′			1.43			1.50	1.73	1.62	1.28	16.3	10.4±0.19	15.8
$20\bar{2}3$	.547	50° 8′			3.13		3.14		3.07	3.37	3.06	52.5		
$21\bar{3}0$	.546	90°										17.4		
$21\bar{3}1$	.566	78° 7′			4.92	4.79	4.46	4.51	4.50	4.33	4.13	114.	6.75±0.05	12.2
$11\bar{2}4$	.592	66° 40′			4.51	4.99	4.44	4.29	4.77	4.17	4.32	90.7	7.57±0.06	14.3
$21\bar{3}2$	.601	67° 10′			1.98	2.24	2.25	2.41	2.15	2.11	2.37	49.2	7.22±0.06	14.0
$10\bar{1}5$	.621	19° 37′					4.32	4.19	4.27	4.25	4.48	96.8	7.18±0.03	13.2

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[8] G. W. Brindley and F. W. Spiers, Proc. Phys. Soc. **46**, 841 (1934), give a set of curves for the quantity $A = \frac{\sin (2\theta-\alpha)}{\sin (2\theta-\alpha)+\sin \alpha}$ (which is the fraction by which the intensity is reduced by absorption in the briquet) as a function of the Bragg angle θ for several values of α, the angle which the incident radiation makes with the face of the briquet.

of reflection when crystal is at temperature of liquid air, and I_{RT}=intensity at room temperature. Then

$$I_{LA}=I_0e^{-2M_{LA}}, \tag{3.1}$$

$$I_{RT}=I_0e^{-2M_{RT}}, \tag{3.2}$$

$$R=I_{LA}/I_{RT}=e^{2(M_{RT}-M_{LA})}, \tag{4}$$

and

$$\log R=2(M_{RT}-M_{LA}). \tag{5}$$

From the equations derived by Zener,[9]

$$M_T=(a_T\cos^2\psi+b_T\sin^2\psi)(\sin\theta/\lambda)^2Q(x), \tag{6.0}$$

where ψ is the angle which the normal to the reflecting plane makes with the C axis of the crystal, $Q(x)$ is the quantization factor and is nearly equal to unity, $x=\Theta/T$, Θ is the characteristic temperature of the metal, T is the absolute temperature, and a_T and b_T are functions of the temperature only.

For a cubic crystal of atoms of one kind, Debye and Waller have shown that

$$M_T=\frac{6h^2T}{mk\Theta^2}Q(x)\left(\frac{\sin\theta}{\lambda}\right)^2. \tag{7}$$

Since M_T is a linear function of T for cubic crystals, we shall assume that it is also a linear function of T for anisotropic crystals. Letting $a_T=a\cdot T$, and $b_T=b\cdot T$, we get

$$M_T=Q(x)T(\sin\theta/\lambda)^2(a\cos^2\psi+b\sin^2\psi). \tag{6.1}$$

Actually Θ is a function of both ψ and T, but this has such a small effect on the value of Q that Θ is assumed to be constant. Moreover, Θ is not known for this alloy, but it can be taken equal to that of pure zinc to a sufficiently good approximation. Combining Eqs. (5) and (6.1), we get

$$\frac{\log R}{(\sin\theta/\lambda)^2}=2(Q_{RT}T_{RT}-Q_{LA}T_{LA})(a\cos^2\psi+b\sin^2\psi)=2\Delta(QT)(a\cos^2\psi+b\sin^2\psi). \tag{8.0}$$

For the $21\bar{3}1$ line,

$$a_T\cos^2\psi_1+b_T\sin^2\psi_1=\frac{T_{RT}\log R_1}{2\Delta(QT)(\sin\theta_1/\lambda)^2}, \tag{8.1}$$

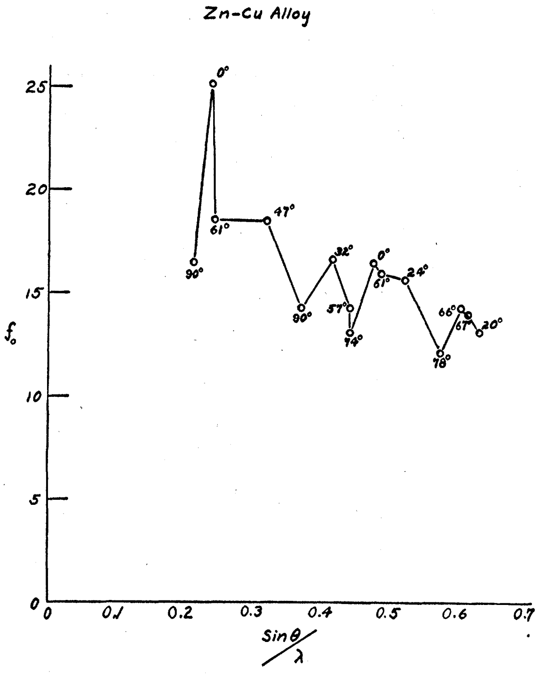

FIG. 3. Relative structure factor for an atom at $T=0$.

and for the $10\bar{1}5$ line,

$$a_T\cos^2\psi_2+b_T\sin^2\psi_2=\frac{T_{RT}\log R_2}{2\Delta(QT)(\sin\theta_2/\lambda)^2}. \tag{8.2}$$

The results of fifteen films and seventy-four microphotometer traces are used in obtaining solutions for a_T and b_T. We get

$$a_T=1.51\pm0.118\text{A}^2$$

and

$$b_T=1.84\pm0.098\text{A}^2.$$

5. DISCUSSION

The individual values of R_1 and R_2 vary over a considerable range, so that the values obtained for a_T and b_T can have no high accuracy. Two facts are to be noted, however. In the first place, the probable errors are sufficiently small that the limiting values of a_T and b_T do not overlap. Secondly, if one uses (a_T-b_T) as a measure of the anisotropy as Jauncey[1] prefers to do, he gets

$$(a_T-b_T)=-0.33\pm0.155\text{A}^2,$$

so that the limiting values of the anisotropy are always negative. Therefore, while the results cannot be said to prove absolutely that b_T is

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[9] C. Zener, Phys. Rev. **49**, 122 (1936).

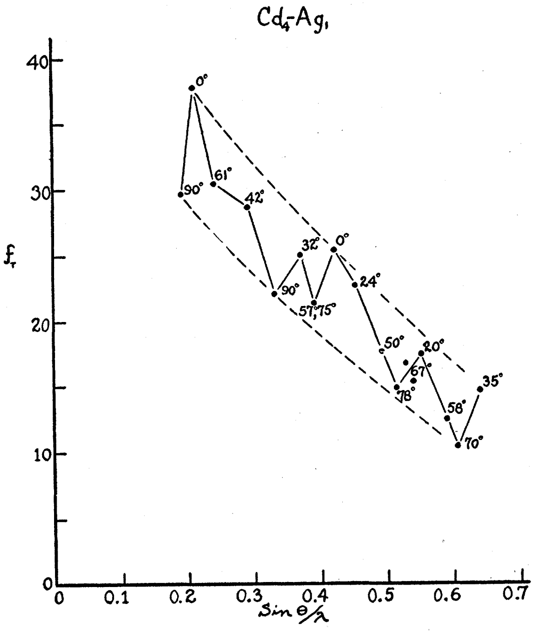

FIG. 4. Atomic structure factor of Cd 80 percent, Ag 20 percent (atomic percent) *vs.* (sin θ)/λ.

greater than a_T, it seems extremely probable that this is the case, and our hypothesis about the vibrations being greater in a direction normal to the *c* axis of the crystal than along it is apparently confirmed.

If we now use a_T and b_T to calculate the relative structure factors reduced to an atom at absolute zero temperature (no correction for dispersion) we get the results shown in Fig. 3. It will be noticed that the results are not essentially different from those for f_T, and the question immediately comes up, "What causes the f values to vary so violently as a function of the orientation angle, ψ?"

The thing which suggests itself first is distortion caused by grinding the crystals. Elastic distortion we can rule out immediately because the effect of elastic distortion is to broaden the lines, and the lines are no broader than those obtained from annealed filings of the alloy or from pure sublimated zinc. Barrett,[10] and Hengstenberg and Mark[11] have also found that cold working a metal has very little effect on the line width. Plastic deformation, in which slipping takes place along certain planes in the crystal, could give rise to highly strained surface layers at points along the slip planes or at fractures, and possibly even to a layer of amorphous material between the slip planes. Amorphous material along the slip planes would introduce an additional absorption factor which would be a function of both θ and ψ. It is also possible that some part of the scattering of the f values is due to electron asymmetry in the atom. Such an idea is consistent with the fact that the spread of the points *decreases* with increasing (sin θ)/λ, which is just what is to be expected if the electron distribution in the atom is asymmetric. If the whole effect is due to electron distribution asymmetry, the effect must necessarily reach down into the inner electron shells, as an asymmetric distribution of the outer two electrons of zinc is insufficient to give the observed change between the f values for $\psi = 90°$ and $\psi = 0°$.

Figure 4 shows some unpublished f_T values obtained by Dr. E. O. Wollan[12] for a Cd-Ag alloy containing approximately twenty atomic percent silver. This alloy also has an axial ratio of 1.56. The situation is almost exactly parallel to that of the Zn-Cu alloy, in that we replace part of the atoms of an element whose crystals have a high axial ratio (1.89) by an element whose atomic number is one less. The alloys were both prepared in the same manner, and the powders treated in the same way. It will be noticed that here again the spread of the points increases as (sin θ)/λ decreases, although the percentage change is somewhat less. Whatever the explanation of this large change is, it is evident that it will suffice for both alloys.

6. ACKNOWLEDGMENTS

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[10] Barrett, Phys. Rev. **47**, 333 (1935).

[11] Hengstenberg and Mark, Zeits. f. Physik **61**, 435 (1930).

[12] E. O. Wollan, Phys. Rev. **53**, 203(A) (1938).