from the experimental shape. The single Landau curve, Fig. 12, also fits less well than the Halpern-Hall theory although the difference here is not so striking. It seems quite interesting that, to a good approximation for these experiments, the entire cosmic-ray spectrum may be replaced by a single energy.

The fact that the peak of the Halpern-Hall curve agrees so well with the experimental curve may be taken as an indication that a small relativistic rise is present (see Table I). Thus our results are in agreement with those of Bowen and Roser who find evidence of saturation in the Halpern-Hall model of anthracene. Our experimental curve does, however, show a small divergence from the theoretical Halpern-Hall curve. The reason for this is not known at present.

CONCLUSION

It appears that the density or polarization effect is observed in NaI(Tl) as well as in anthracene (Bowen-Roser) and that a small relativistic rise probably exists in NaI(Tl). It would be desirable to improve the measurements of absolute energy-loss, the statistical accuracy of the data, and to use monoenergetic mesons, so that folding-in of the cosmic-ray spectrum will become unnecessary. We hope to do further work along all these directions. It is interesting that NaI(Tl) appears to be linear in the range of high meson energies in the cosmic rays, a result that might have been anticipated from previous experiments with other charged particles.

We wish to thank Dr. Sidney Drell for his very kind help in considering many of the theoretical aspects of this problem and also for his independent calculations of energy loss. We also wish to thank Dr. J. A. McIntyre for help in packaging the NaI(Tl) crystals. Finally we appreciate greatly the kindness of Dr. Burton Moyer, of the University of California, in lending us, from time to time, his Po-Be source.

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Electron Diffraction from Small Crystals*

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Small crystals of silver and silver bromide were studied by electron diffraction. Small crystals of these materials are of interest because published experimental and theoretical considerations indicate changes in their structure which may occur. Since the diffraction theory which is applicable to large crystals cannot always be used in interpreting the photographs from materials of small size, computations were made for crystal structures and shapes which might be expected for silver and silver bromide. As a result of the computations, it was found that positions of diffraction peaks of substances having the sodium chloride structure depend on the crystal shape. It was also shown that the determination of particle size by the usual method of the Scherrer equation may give values which are much too small. Comparison of experimental and theoretical diffraction effects indicates that small silver particles have the same structure as the large particles, but that there is a real contraction of the lattice in the smaller particles which amounts to 2.7 percent for particles with a diameter of about 31A. The small silver bromide particles have the same structure as the large particles, and an apparent expansion of the silver bromide lattice of about 1.0 percent appears to be best explained not as an expansion but as a particle-shape effect which changes the position of the diffraction peak. The crystals appear to be plates bounded by (111) faces, just as in many photographic emulsions, although this is not the usual form of crystals having this structure.

INTRODUCTION

BECAUSE there are differences between the surface and the internal properties of crystals, it is of interest to compare the characteristics of large crystals with those of very small crystals in which the surface to volume ratio is relatively high. Scattering of electrons from small crystals is sufficiently strong to permit an electron-diffraction study to be made. Boswell[1] has recently published some results obtained by electron diffraction from small crystals of alkali halides, gold, and bismuth. He reports a decrease in lattice constant with decrease in particle size in the diameter range below 100A. The decrease is attributed to a surface-tension effect predicted by Lennard-Jones and Dent.[2]

The substances studied here are silver and silver bromide. Silver is of particular interest in view of Quarrell's[3] observation of many cubic close-packed metals which appeared to begin their growth with the hexagonal close-packed structure. A theoretical study of the lattice energies of the silver halides by Huggins[4] indicates a small difference in the energies of silver

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[1] F. W. C. Boswell, Proc. Phys. Soc. (London) **A64**, 465 (1951).

[2] J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. (London) **A121**, 247 (1928).

[3] A. G. Quarrell, Proc. Phys. Soc. (London) **49**, 279 (1937).

[4] M. L. Huggins, J. Chem. Phys. **11**, 412 (1943).

bromide in the sodium chloride type of structure and in the zinc sulfide types of structure, and he suggests that under some circumstances, particularly at the surface, a transition from the normal sodium chloride structure may be expected. Silver bromide is also of interest because of its photographic behavior and because of its abnormally large number of lattice defects.

In interpreting electron-diffraction patterns from thin films of gold and copper, Germer and White[5] have calculated the diffraction effects to be expected from small spherical particles of face-centered cubic structure in random orientation. This type of analysis has been extended to crystals of various structures, shapes, sizes, and orientations to permit more detailed interpretation of the experimental results.

EXPERIMENTAL

Small crystals of silver or silver bromide were formed by vacuum evaporation in the electron-diffraction instrument. The deposits were collected on thin cellulose membranes and were observed by transmission. No attempt was made to determine the average thickness of the deposits, since it was considered that the size of the crystals was the important factor and this could best be determined from the diffraction patterns. A calibrating substance, usually potassium bromide, was formed on the reverse side of the cellulose support by vacuum evaporation.

It was found that a considerable concentration of small particles of silver could be readily produced. Control of the amount of material evaporated could be conveniently managed merely by observing the silver-diffraction pattern on the fluorescent screen. Diffraction patterns from crystallites having diameters of about 30A could be seen clearly. However, this was not the case with silver bromide, which tended to form a small number of relatively large particles.

It was possible to obtain satisfactory microphotometer traces of the (111) reflection from the small silver particles and to compare its position with the lines of the potassium bromide calibrating substance, whose lattice constant was assumed to be 6.586 Kx as given by Wyckoff.[6] To determine the breadth of the reflection at half-maximum intensity, it was assumed that density on the photographic plate was proportional to exposure. The positions of many (111) reflections from silver particles of various sizes were also determined visually on a plate-measuring device. The Bragg spacing of the (111) reflection was as small as 2.292 Kx in some cases, compared to the value for large particles of 2.355 Kx. This difference in values agrees with the observations of Boswell[1] on many materials, although the decrease of 2.7 percent is larger than in any of the materials which he studied.

The half-maximum intensity breadth of a reflection may be conveniently expressed as $2\Delta\theta/2\theta$, where 2θ is the scattering angle for the reflection and $2\Delta\theta$ is the angular breadth of the reflected beam at half-maximum intensity.

For the broadest (111) reflection observed, the half-intensity breadth expressed as $2\Delta\theta/2\theta$ was about 0.11. The geometrical breadth due to instrumental factors was about 0.02.

Since most of the patterns of small silver bromide particles were not sufficiently strong to give good microphotometer traces, the peak position of the innermost (200) ring was determined by visual estimation. There was considerable variation in the results obtained for particles of a given apparent size, but the observations of a large number of plates were used in determining the final results. It was found that the Bragg spacing of the reflection increased with decreasing particle size, quite the opposite effect from that occurring with silver and from that observed by Boswell for a large number of substances having the sodium chloride structure. The maximum effect observed was an increase of about 1.0 percent. This unusual behavior made it desirable to reconsider the experimental conditions for a possible source of the discrepancy. The only possibility which suggested itself was that some of the potassium bromide calibrating substance had come in contact with the silver bromide on the support and had expanded the silver bromide lattice by solid solution or by strained epitaxial growth of silver bromide on the potassium bromide. To detect any lattice expansion by the calibrating material, several exposures were made using, in place of KBr, LiF, in which each ion is smaller than the corresponding ions in silver bromide. Since, in this case, the Bragg spacing of the (200) silver bromide reflection again increased with decreasing particle size, it was concluded that the behavior was characteristic of silver bromide.

One particularly good plate having an intense, broad silver bromide pattern could be examined with the microdensitometer, and the measurement gave a Bragg spacing which was 0.8 percent greater than the normal value for large particles and a half-intensity breadth of about $2\Delta\theta/2\theta=0.08$.

CALCULATED DIFFRACTION EFFECTS FOR SMALL CRYSTALS

Germer's[7] experiments on the diffraction of electrons from small metal particles gave results which could not be interpreted readily in terms of diffraction theory for large particles. However, Germer and White[5] were able to explain some of the effects on the basis of calculations, using the gas-scattering equation, which gives the intensity of electrons scattered from small groups of atoms in random orientation. The equation for this scattering is of the form given by Debye[8] for the scat-

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[5] L. H. Germer and A. H. White, Phys. Rev. **60**, 447 (1941).

[6] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. I.

[7] L. H. Germer, Phys. Rev. **56**, 58 (1939).

[8] P. Debye, Ann. Physik (4) **46**, 809 (1915).

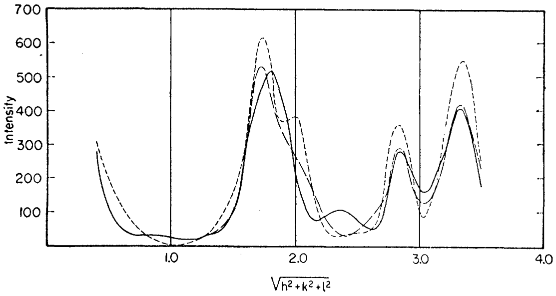

FIG. 1. Calculated diffraction patterns for silver crystals. --- Sphere of 201 atoms, cubic structure; — — Plate of 183 atoms, cubic structure; —— Plate of 183 atoms, hexagonal structure.

tering of x-rays and may be written as:

$$I=f(\theta)\sum_j\sum_k f_jf_k\sin(4\pi l_{jk}\sin\theta/\lambda)/(4\pi l_{jk}\sin\theta/\lambda),$$

where θ is half the scattering angle; $f(\theta)$ is a monotonically decreasing function on which are superimposed the maxima and minima of the double summation; f_j and f_k are the scattering amplitudes of the jth and kth atoms; l_{jk} is the separation of the jth and kth atoms within an individual crystal; and λ is the wavelength of the radiation. This relation has been used here in making similar computations and the values of $f(\theta)$, f_j, and f_k have been made equal to unity.

In addition, it was desirable to consider the diffraction effects to be expected from crystals in uniaxial orientation in the direction of the electron beam. This type of orientation will occur when crystals having well-developed faces are deposited on a smooth support, the face being always parallel to the support and perpendicular to the electron beam. In this case, it can be shown that the scattered intensity may be written:

$$I=f(\theta)\sum_j\sum_k f_jf_k\cos[2\pi S_{jk}(1-\cos 2\theta)/\lambda]\times J_0(2\pi D_{jk}\sin 2\theta/\lambda),$$

where the quantities are defined as above, and in addition S_{jk} and D_{jk} are the components of separation of the jth and kth atoms along the direction of the electron beam and perpendicular to the direction of the electron beam, respectively; and J_0 is the Bessel function of zero order. In the case of a single layer of atoms, S_{jk} is zero, and the summation contains only the Bessel function. Also, for small particles of only a few layers thickness and at small angles, $S_{jk}(1-\cos 2\theta)$ is so small that the intensity is dependent only on D_{jk}.

Since the position, intensity, and breadth of a diffraction line can be determined experimentally, the dependence of these characteristics on particle size, shape, and structure was calculated. For the close-packed cubic structure and particles of spherical shape, Germer and White[5] made the calculations plotted in Fig. 3 of their paper for particles of many sizes. For 379 atoms, corresponding to an external diameter of 26.0A for silver, having the normal lattice constant, the pattern begins to look much like that for infinitely large particles. The first peak occurs at a position 1.73 in terms of $(h^2+k^2+l^2)^{\frac{1}{2}}$ and has a half-intensity breadth of 0.13. If the Scherrer[9] equation is used to compute the particle size from this value of line breadth, the particle size obtained is too small. For example, if the coefficient 1.11 is used in the Scherrer equation, which Patterson[10] computed for a spherical particle, the resultant size is 20.1A. If Boswell's scheme of using the coefficient 0.9 is followed, a particle size of only 16.4A is obtained.

In order to determine the effect of particle shape and structure on the diffraction curves, computations were made here for three kinds of particles in random orientation: a sphere of 201 atoms (exterior diameter of 21.2A for silver) in the cubic close-packed structure, a plate of 183 atoms consisting of three 61-atom close-packed layers (having breadth of 27A and thickness of 7.6A) in cubic stacking, and a plate of 183 atoms consisting of three 61-atom close-packed layers in hexagonal stacking. The number of atoms in these particles is apparently somewhat less than in the smallest silver particles observed experimentally, but this was done to reduce somewhat the very lengthy computations involved. The results are shown in Fig. 1. For both the cubic structures, the first maximum occurs at $(h^2+k^2+l^2)^{\frac{1}{2}}=1.73$, and the next peak at $(h^2+k^2+l^2)^{\frac{1}{2}}=2.00$ begins to appear. It is difficult to distinguish between the spherical and platelike shape from the diffraction patterns. The hexagonal structure gives a peak position and shape which are quite different from those of the cubic structure. Computations for the platelike crystals with uniaxial orientation showed a first maximum of intensity only at $(h^2+k^2+l^2)^{\frac{1}{2}}=2.83$. The diffraction patterns from the smallest particles of silver observed showed partial resolution of the (200) peak, thereby eliminating the possibility of a hexagonal structure in these crystals. The smallest particles of silver observed were therefore of the usual cubic structure, the lattice constant was about 2.7 percent smaller than that of bulk material, and the size was that expected for spheres of about 31A diameter.

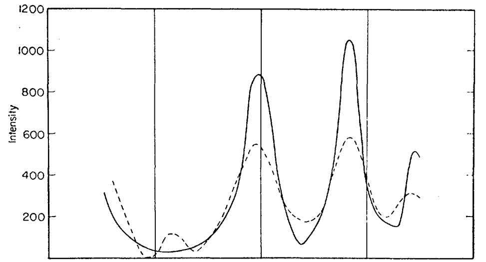

FIG. 2. Calculated diffraction patterns from crystals with sodium chloride structure. Hexagonal plates bounded by (111) faces. --- Four 19-atom layers (intensity scale expanded four times); —— Six 61-atom layers.

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[9] P. Scherrer, Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, No. 2, p. 98 (1918).

[10] A. L. Patterson, Phys. Rev. **56**, 972 (1939).

Computations were also made for the diffraction patterns to be expected for small crystals of the NaCl structure in random orientation for flat plates with (100) faces and with (111) faces, as well as for more nearly spherical particles. To simplify the computations, $f(\theta)$, f_j, and f_k were again taken as unity. This means that the scattering of the positive and negative ions in the structure is assumed to be equal. In contrast with the situation for the silver structure, the particle shape has a definite effect on the position of the first maximum. In Fig. 2, there is shown the diffracted intensity from hexagonal-shaped plates containing alternate (111) planes of anions and cations, which is often the shape of grains observed in photographic emulsions. The two curves are for the cases of four 19-atom layers (20A in breadth and 7.8A thick) and for six 61-atom layers (37A in breadth and 11.2A thick). The (200) peak positions are shifted to smaller values of angle from that for large particles and occur at $(h^2+k^2+l^2)^{\frac{1}{2}}=1.97$ and $(h^2+k^2+l^2)^{\frac{1}{2}}=1.98$ for the 76-atom and 366-atom particles, respectively. Further computations indicate, for about 100 atoms in the particle, that the peak position shifts to smaller angles the greater the departure from spherical toward plate shape. The effect of the (111) plate shape is to give an apparent increase in lattice constant.

In Fig. 3 are given curves for the diffraction from plates in random orientation made up of (100) planes in the NaCl structure. The cases considered are for two 25-atom layers in a square array (15.4A edge length and 6.8A thick) and for three 25-atom layers (15.4A edge length and 9.7A thick). Here, the (200) peak positions are shifted to larger values of angle from that for large particles and occur at

$$(h^2+k^2+l^2)^{\frac{1}{2}}=2.02 \quad \text{and} \quad (h^2+k^2+l^2)^{\frac{1}{2}}=2.01$$

for the 50-atom and 75-atom arrays, respectively. Computations for small crystals having uniaxial orientation about the (100) and (111) axes show maxima which are not noticeably displaced from those observed for large crystals with the same orientations.

Hence, the apparent increase of lattice parameter of small silver bromide crystals is the result of their crystallization as plates bounded by (111) faces. Electron micrographs of 350A silver bromide crystals formed by vacuum evaporation were prepared to check this conclusion concerning crystal shape. There was a definite tendency for the hexagonal shape to occur, although regular hexagons were observed in only about one crystal in ten. It is interesting that this shape of the silver bromide crystals occurs, since Mitchell[11] suggests that crystallization with (100) faces would be expected except when the crystals are formed from solutions under special conditions. Since the half-intensity breadth of the experimental diffraction curve of the smallest particles is only about half as great as that calculated for the 366-atom particle, the crystals observed experimentally must be somewhat larger than 500 atoms. Another conclusion which is derived from consideration of the curves in Fig. 3 is that the apparent decrease in lattice constant of small crystallites of the alkali halides observed by Boswell may be caused, at least in part, by their crystallization as plates bounded by (100) faces.

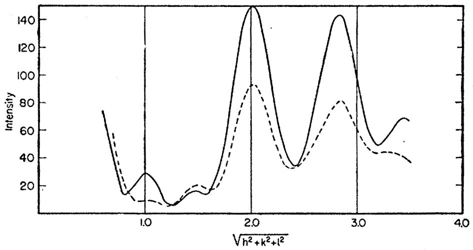

FIG. 3. Calculated diffraction patterns from crystals with sodium chloride structure. Square plates bounded by (100) faces. - - - Two 25-atom layers; —— Three 25-atom layers.

Possible reasons for an actual lattice expansion of small particles of silver bromide were considered. According to Huggins, an expansion of the lattice would be expected in the transition from the NaCl to the ZnS cubic structure. However, the relative intensities of the diffraction lines in these two structures are quite different, and the existence of the NaCl structure is indicated by the strong (200) reflection and the absence of the (111) reflection. The presence of Frenkel defects in the crystals would cause a lattice expansion. If we assume, according to Lawson,[12] that the production of 2 percent Frenkel defects in silver bromide causes a volume increase of 0.2 percent, then a lattice constant increase of 1 percent would require an impossible number of about 30-percent defects. The particle-shape effect appears to give the most logical explanation for the peak position observed in the silver bromide patterns, but there may be in addition real changes in the lattice constant which are obscured by the shape effect.

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[11] J. W. Mitchell, "The nature of sensitivity centers and the formation of the latent image in the grains of chemically non-sensitized emulsion," contribution to Paris Photographic Conference, 1951 (to be published).

[12] A. W. Lawson, Phys. Rev. 78, 185 (1950).