X-Ray Scattering Effects Due to Localized Static Lattice Defects

CHARLES W. TUCKER, JR., AND PETER SENIO
Knolls Atomic Power Laboratory, General Electric Company, Schenectady, New York*
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Theoretical calculations by Huang show that elastic singularities in a crystalline lattice should produce four specific x-ray scattering effects which include diffuse scattering and an artificial temperature factor. All four of the effects are present in neutron-irradiated crystals of boron carbide, diamond, silicon carbide, and magnesium oxide. Thus the model and calculations of Huang are qualitatively confirmed. It is suggested that it may be possible to determine more precisely the nature of the lattice distortions around localized static lattice defects from a detailed study of the diffuse scattering.

INTRODUCTION

THE literature pertaining to the scattering of x-rays by distorted crystals is very large and some of it dates back to the early days of the development of x-ray diffraction theory.[1] However, much of this literature is concerned with distortions and size limitations which upset the coherence of the scattering between the unit cells of which the crystal is composed. This broadens and changes the shape of the coherent scattering peaks, the Bragg reflections, and the problem becomes that of deducing from the alterations of the peak shapes the nature of the distortions and the size distributions present. With the important exception of the effect of temperature on x-ray scattering, the case in which the distortions are due to small localized lattice defects has not been nearly as extensively studied. Since this paper is concerned with localized *static* lattice defects, temperature effects will not be considered, although reference will be made to them. Localized static lattice defects will be interpreted to mean defects which are small in three dimensions, *viz.*, interstitials, vacancies, oversize atoms, or agglomerates of only several atoms at most. Thus scattering due to dislocations, for example, is excluded.

THEORETICAL

Theoretical calculations of the x-ray scattering by a crystalline lattice containing a random distribution of localized static lattice defects are rather few. While we shall consider only the detailed treatment of the problem given by Huang,[2] the literature will be reviewed briefly.

Laue[3] refers to the problem in his treatment of the x-ray scattering by a solid solution in which the component atoms are of different sizes, but does not give detailed calculations. Ekstein[4] and Matsubara[5] examine the case in which the lattice atoms are given small displacements from their sites in a perfect lattice, expressing the scattering by the distorted lattice by the first two terms in a Taylor's series. Ekstein takes as an example of the displacements around a defect the classical elasticity problem of the displacements in a hollow sphere due to a pressure in the internal cavity.[6] Matsubara obtains his displacements by minimizing the strain energy of the lattice as a function of the displacements. For the case of defects producing displacements over rather large distances, Matsubara points out that his treatment becomes equivalent to that of Ekstein. Both authors show that the defects lead to the production of diffuse maxima surrounding the sharp Bragg reflections at the reciprocal lattice points. Other than this specific x-ray effects are not discussed.

Warren, Averbach, and Roberts[7] discuss an atomic size effect in solid solutions due to the difference in size of solvent and solute atoms. Their calculations predict an asymmetry in the diffuse scattering due to the size effect such that there is an increase in scattering on one side of a reciprocal lattice point and a decrease on the other side. The magnitude of this effect depends not only on the difference in size of the solvent and solute atoms, but also on the difference in their atomic scattering powers. Interest in the present paper will be in distortions of more general types for which the difference in scattering power of matrix and defect atoms is either zero or ignored. Therefore, the size effect computed by Warren, Averbach, and Roberts will not be considered further here.

Zachariasen[8] has given a general theory of x-ray scattering by displacement disorders in a crystal. In this theory displacement of the atoms from their normal lattice sites leads to a decrease in the effective scattering power per unit cell and to the production of diffuse scattering surrounding the reciprocal lattice points.

While detailed calculations based on the previously mentioned work, particularly that of Zachariasen,[8] Ekstein,[4] and Matsubara[5] might well be used in de-

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[1] For a recent survey of this field, the monograph by A. J. C. Wilson, *X-ray Optics—The Diffraction of X-rays by Finite and Imperfect Crystals* (Methuen and Company Ltd., London, 1949) is recommended.

[2] K. Huang, Proc. Roy. Soc. (London) **A190**, 102 (1947).

[3] M. v. Laue, *Röntgenstrahl-Interferenzen* (Edwards Brothers, Inc., Ann Arbor, 1943), p. 179.

[4] H. Ekstein, Phys. Rev. **68**, 120 (1945).

[5] T. J. Matsubara, Proc. Phys. Soc. Japan **7**, 270 (1952).

[6] A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), p. 142.

[7] Warren, Averbach, and Roberts, J. Appl. Phys. **22**, 1493 (1951).

[8] W. H. Zachariasen, *Theory of X-ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, 1945), Chap. IV.

termining the x-ray effects produced by localized static lattice defects, a rather complete treatment of a fairly general problem has already been given by Huang.[2] Specifically, Huang considered the x-ray scattering by a face-centered cubic lattice containing a random distribution of elastic singularities which produce elastic displacements of the surrounding atoms of the form $u=c/r^2$, where u is the displacement of an atom a distance r from a singularity of "strength" c. Actually, this equation is correct only for an infinite medium. As will be discussed later, the form for a finite medium changes the quantitative value of c but does not change the qualitative nature of the x-ray scattering effects to be considered. In any case, Huang took the displacements for the infinite medium as the basis of a model for a dilute solid solution in which the solute atoms have a different atomic radius than that of the solvent atoms. However, the model can be interpreted more generally if the solute atom is considered to be any defect of atomic dimensions which produces radial elastic displacements of the form $u=c/r^2$ and whose concentration is small.

Huang's analysis starts with the conventional expression for the scattering of x-rays by an assemblage of n atoms, namely,

$$Sf^2|\textstyle\sum_n \exp i(\boldsymbol{\xi}\cdot\mathbf{r}_n)|^2, \tag{1}$$

where S is the scattering calculated by Thomson for a single electron and f is the atomic scattering factor. The vector $\boldsymbol{\xi}$ is given by $2\pi/\lambda(\mathbf{n}-\mathbf{n}_0)$ where $\mathbf{n}_0$ and $\mathbf{n}$ are unit vectors in the direction of the incident and the scattered waves, respectively, and λ is the wavelength of the x-rays. The vector $\mathbf{r}_n$ locates the nth atom and is given by

$$\mathbf{r}_n=\mathbf{a}_n+\textstyle\sum_i \mathbf{u}(\mathbf{a}_n-\mathbf{a}_i), \tag{2}$$

where $\mathbf{a}_n$ locates the nth atom in the undistorted lattice and $\mathbf{u}(\mathbf{a}_n-\mathbf{a}_i)$ represents the vector displacement of the nth atom due to the ith defect. Substituting Eq. (2) in expression (1) and analyzing the problem on the basis of a statistically uniform distribution of defects, which distribution may fluctuate locally, Huang shows that the scattering becomes

$$Sf^2\textstyle\sum_n\sum_m \exp\{i\boldsymbol{\xi}\cdot[\mathbf{a}_n-\mathbf{a}_m+p\sum_i^{\text{all sites}}(\mathbf{u}(\mathbf{a}_n-\mathbf{a}_i)-\mathbf{u}(\mathbf{a}_m-\mathbf{a}_i))]\}\times\{1-\tfrac{1}{2}(1-\delta_{nm})(p-p^2)\times\sum_i^{\text{all sites}}[\boldsymbol{\xi}\cdot(\mathbf{u}(\mathbf{a}_n-\mathbf{a}_i)-\mathbf{u}(\mathbf{a}_m-\mathbf{a}_i))]^2\}, \tag{3}$$

where p is the concentration of defects. The double summation arises in forming the square as required by expression (1). Substituting the explicit form for the displacements, namely, $\mathbf{u}=c\mathbf{r}/|\mathbf{r}|^3$, Huang then forms the indicated summations within the double summation signs in expression (3). These summations are resolved into three separate summations of which two are relatively simple but the third quite complex. Finally Huang obtains for the scattered intensity:

$$Sf^2\sum_n\sum_m\left[1-(1-\delta_{nm})(p-p^2)\frac{4\pi c^2|\boldsymbol{\xi}|^2}{3\rho_0 v}\right]\times\exp[i\boldsymbol{\xi}\cdot(\mathbf{a}_n-\mathbf{a}_m)]\left(1+\frac{4\pi cp}{3v}\right)+Sf^2(p-p^2)\times\frac{\pi c^2|\boldsymbol{\xi}|^2}{2v}\sum_n\sum_m(1-\delta_{nm})\left\{\frac{2\sin^2\Theta}{|\mathbf{a}_n-\mathbf{a}_m|}-\frac{(2\rho_0)^2\sin^2\Theta}{3|\mathbf{a}_n-\mathbf{a}_m|^3}-\frac{2(2\rho_0)^2\cos^2\Theta}{3|\mathbf{a}_n-\mathbf{a}_m|^3}\right\}\exp[i\boldsymbol{\xi}\cdot(\mathbf{a}_n-\mathbf{a}_m)]\left(1+\frac{4\pi cp}{3v}\right), \tag{4}$$

where v is the atomic volume, Θ the angle between $\boldsymbol{\xi}$ and $\mathbf{a}_n-\mathbf{a}_m$, and ρ_0 a cutoff which is difficult to evaluate exactly but which is of the order of atomic dimensions. In spite of the complexity of expression (4) certain features of the scattering are easy to recognize, remembering that the scattering by a stationary lattice without defects would be

$$Sf^2\sum_n\sum_m\exp[i\boldsymbol{\xi}\cdot(\mathbf{a}_n-\mathbf{a}_m)]. \tag{5}$$

The first term of expression (4) gives the usual sharp crystalline or Bragg reflections except that their positions and intensities are altered. The term $(4\pi cp)/(3v)$ in the exponent shows that the lattice has expanded isotropically as though a strain of this magnitude had been imposed upon the lattice. The quantity in the large square brackets can be regarded as the first two terms in the Taylor expansion of $\exp(-x^2)$. In this case, since $|\boldsymbol{\xi}|=(4\pi/\lambda)\sin\theta$, the quantity may be written in the form $\exp[-k(\sin^2\theta)/\lambda^2]$, where k is a constant, θ the Bragg angle, and λ the wavelength of the x-rays. Now the well known temperature factor for x-ray scattering by crystals, namely, $\exp[-B(\sin^2\theta)/\lambda^2]$, contains the same functions of θ and λ. However, the quantity B in the temperature factor depends on the temperature of the crystal whereas the constant k in the factor for localized static lattice defects is independent of temperature. This provides an important test for separating the x-ray effects due to the two factors. Owing to the functional similarity of the two factors, that for localized static lattice defects will be called the artificial temperature factor. Since the true temperature factor reduces the intensities of the Bragg reflections without altering their shapes, it is clear that the artificial temperature factor will produce the same effects.

The second term of expression (4) represents the diffuse scattering and is crudely analogous to temperature diffuse scattering, except that it is not, of course, temperature sensitive. The appearance of the same exponential factor as occurs in the first term assures that this scattering is located in the vicinity of the Bragg reflections, that is, surrounds the reciprocal lattice points. While the calculation of the detailed nature of

this diffuse scattering is complex, Huang shows that the diffuse scattering for dilute solid solutions is comparable in intensity and extension in reciprocal space to thermal diffuse scattering at low temperatures.

To summarize, the calculations of Huang predict theoretically the following x-ray scattering effects from a lattice containing a random distribution of defects which produce elastic displacements of the form $u=c/r^2$: (1) an isotropic expansion of the lattice; (2) an artificial temperature factor; (3) no broadening of the Bragg reflections; (4) diffuse scattering surrounding the reciprocal lattice points. It is the purpose of the next section to show that these effects are all observed experimentally.

Before proceeding to a discussion of the experimentally observed x-ray effects, however, it is appropriate to consider a matter which alters the results of Huang quantitatively in a way which may ultimately prove to be important, although it does not alter the results qualitatively. This matter concerns the use by Huang of the equation $u=c/r^2$ to express the displacements of the atoms around a defect. This equation is strictly applicable only to the case of an infinite medium. Eshelby[9] has given a very general analysis of the effect of neglecting the finite nature of the medium in problems using the elastic model for defects. In the problem solved by Huang it is stated by Eshelby that, due to the neglect of the surface term in the expression for the displacements, the constant c should be replaced by $c\gamma$, where $\gamma=3(1-\sigma)/(1+\sigma)$ and σ is Poisson's ratio. This increases the effective value of c by a factor of 1.8 or 1.5 depending on whether the value taken for Poisson's ratio is $\frac{1}{4}$ or $\frac{1}{3}$. Thus the magnitude of the effects predicted by Huang is increased by a significant amount.

EXPERIMENTAL

The isotropic lattice expansion and lack of line broadening predicted by Huang's calculations are confirmed by a very wide experience with solid solutions. Actually, as Tucker and Sampson[10] have pointed out, Huang's analysis, when corrected for the effect of the free surface term, predicts Vegard's law. This empirical law states that when two materials of the same crystal structure form a continuous series of solid solutions, the plot of lattice parameter *versus* composition is a straight line joining the parameters of the pure materials. While Vegard's law is surely an idealization, it forms a reasonable first approximation in many systems. The absence of line broadening in solid solutions is an experimental fact of long standing. Quite appreciable solubilities exist in some cases for which the radius mismatch between solvent and solute atoms amounts to 10 to 15%. Since the distortions around the solute atoms are certain to be large in such cases, the absence of line broadening provides a good test of Huang's calculations. No attempt has yet been made to look for the diffuse scattering, but the artificial temperature factor predicted by Huang's calculations for solid solutions has been reported by Coyle and Gale[11] in a gold-copper alloy.

While the lattice expansion, the absence of line broadening, and the presence of an artificial temperature factor in the gold-copper alloy studied by Gale provide evidence for the correctness of Huang's calcluations for the case of solid solutions, neutron irradiated single crystals provide the basis for a complete test of the calculations. In certain irradiated crystals all four of the predicted effects are found simultaneously. The reason that the effects are so pronounced in irradiated crystals is that the "strength" of the defects, as given by the constant c in $u=c/r^2$, is much greater for defects such as interstitials, vacancies, and foreign atoms (particularly the noble gases) than for substitutional foreign atoms in a solid solution. Since the constant c appears as a square in the terms involving the artificial temperature factor and the diffuse scattering in expression (4), the magnitude of these effects will depend strongly on the value of c.

Thus far the effects have been observed in irradiated single crystals of boron carbide, diamond, silicon carbide, and magnesium oxide. The case most studied has been that of boron carbide and a detailed account of these studies has been published elsewhere.[12] Most of the radiation damage produced in boron carbide is due to the reaction of the B^{-10} nucleus with thermal neutrons to form He^{-4} and Li^{-7} nuclei which then dissipate 2.3 Mev of kinetic energy in the lattice in ionization and bumping collisions. The lattice expansion and artificial temperature factor are highly anisotropic in irradiated boron carbide. However, it was possible to identify an anisotropic defect in the irradiated crystal structure by means of Fourier analysis of the Bragg intensities which accounted for the anisotropy of these effects. Work is in progress to generalize the calculations of Huang to the case of anisotropic defects. While this work is not yet complete, there is no indication that the effects will be qualitatively different from those predicted by Huang. The diffuse scattering effect is observed to a very extreme degree in irradiated boron carbide. Further, this diffuse scattering is temperature insensitive as the theory requires. The absence of broadening in the Bragg reflections is apparent in Laue photograms even for heavily irradiated crystals. Thus irradiated boron carbide exhibits all of the effects predicted by Huang.

The x-ray effects may also be seen in irradiated diamond, silicon carbide, and magnesium oxide crystals, although the artificial temperature factor is not very strong in magnesium oxide. Laue patterns illustrating the diffuse scattering produced in diamond, for example, are shown in Figs. 1 and 2. The diffuse spots

[9] J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).
[10] C. W. Tucker, Jr., and J. B. Sampson, Acta Metallurgica **2**, 433 (1954).
[11] R. A. Coyle and B. Gale, Acta Cryst. **8**, 105 (1955).
[12] C. W. Tucker, Jr., and P. Senio, Acta Cryst. **8**, 371 (1955).

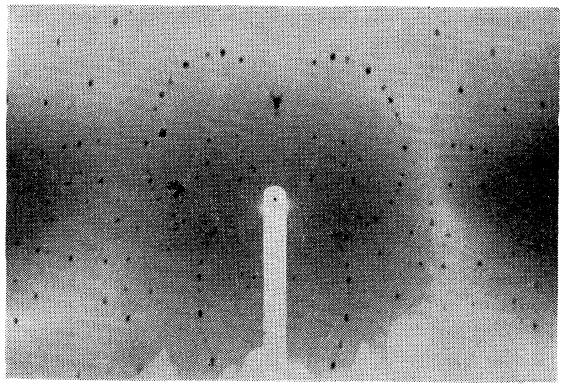

FIG. 1. Laue pattern of unirradiated diamond crystal using unfiltered copper x-radiation. Incident x-ray beam approximately parallel to threefold axis of crystal.

adjacent to and surrounding some of the Laue spots[13] in Fig. 2 show the diffuse scattering due to the defects produced by the irradiation. While the artificial temperature factor is not particularly apparent in Fig. 2, it is quite evident in Laue patterns (not shown) of irradiated silicon carbide. Lattice expansions[14] of the order of 1% are observed in irradiated diamond and silicon carbide, while that in magnesium oxide is about 0.1%. Thus all of the x-ray effects found in irradiated boron carbide are also observed in other irradiated crystal structures, showing that the effects are not peculiar to crystals undergoing fission type reactions.

The occurrence in boron carbide, diamond, silicon carbide, and magnesium oxide of the four x-ray effects predicted by the calculations of Huang provides good evidence that the elastic model used by Huang is a valid model for a crystal containing localized static lattice defects. It does not follow, however, that the effects will always be observed. For example, no diffuse scattering was found in irradiated silicon and germanium. But, since no lattice expansion has been observed in these substances,[14] it appears that there are very few defects of the type which produce the x-ray effects. Similarly, in metals the lattice expansions, in general, are quite small.[10] These observations fit in well with the widely accepted notion that the activation energy for the motion of isolated interstitials or vacancies in metals is rather low. Thus annealing of the main source of defects which could produce the x-ray effects occurs, in metals, at temperatures below room temperature. The crystals in which the x-ray effects have thus far been observed all possess high melting points which are indicative of tight bonding. It would not be expected that the activation energy for the decay of the defects in these crystals would be low. Actually, the anisotropic defect responsible for most of the x-ray effects in irradiated boron carbide was found to anneal in the temperature range of 700 to 900°C.[12]

Accepting a qualitative connection between the calculations of Huang and the observed x-ray effects in irradiated crystals, it becomes clear that it may be possible to learn something of the nature of the distortions in irradiated crystals from a detailed study of the x-ray effects. In this connection it appears most hopeful to study the diffuse scattering, for it is this scattering in the case of thermal effects which has been used many times[15] to determine the elastic constants of crystals and which recently has even been used to work back to the elastic vibration spectrum of copper.[16] However, it must be remembered that the diffuse scattering caused by static lattice defects is due to the distortion of the lattice around the defects rather than to the defects themselves. At the present time there is a discrepancy between theory and experiment regarding the diffuse scattering. Huang's theory predicts that the diffuse scattering around a reciprocal lattice point has roughly the shape of a lemniscate whose axis is parallel to the vector from the origin to the reciprocal lattice point and whose center lies at the reciprocal lattice point. Detailed work with boron carbide and other crystals has shown that the diffuse scattering has roughly the shape of an ellipsoid. This discrepancy may mean that the displacements around the defects deviate from the form $u=c/r^2$ assumed by Huang or that replacement of c by $c\gamma$ as suggested by Eshelby[9] is not valid for the diffuse scattering term. Further theoretical and experimental work is necessary to work out the quantitative aspects of the diffuse scattering.

CONCLUSIONS

The theoretical calculations of Huang show that a lattice containing a random distribution of elastic

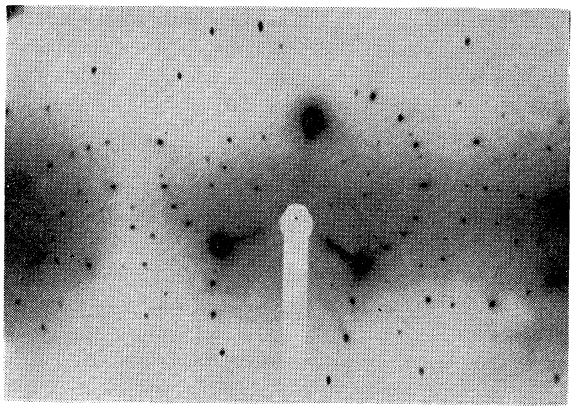

FIG. 2. Laue pattern of neutron irradiated diamond crystal using unfiltered copper x-radiation. Integrated thermal neutron flux 2×10^{20} neutrons/cm^2. Incident x-ray beam approximately parallel to threefold axis of crystal.

[13] Only those planes at or near the Bragg setting for reflection of the very strong characteristic $K\alpha$ or $K\beta$ radiation from the target show the diffuse scattering.

[14] W. Primak, Phys. Rev. 95, 837 (1954).

[15] See, for example, G. N. Ramachandran and W. A. Wooster, Acta Cryst. 4, 431 (1951).

[16] E. H. Jacobsen, Phys. Rev. 97, 654 (1955).

singularities which produce displacements of the form $u=c/r^2$ will scatter x-rays with the following effects: (1) an isotropic expansion of the lattice; (2) an artificial temperature factor; (3) no broadening of the Bragg reflections; (4) diffuse scattering surrounding the reciprocal lattice points.

While the lattice expansion and absence of line broadening have been widely observed in solid solutions, the artificial temperature factor has been observed only once and the diffuse scattering has not yet been observed in solid solutions. However, all four of the effects have been observed in certain neutron irradiated crystals, namely, boron carbide, diamond, silicon carbide, and magnesium oxide. The presence of the effects in these crystals is attributed to the defects produced during irradiation. The fact that the effects are readily observed in irradiated crystals is due to the much greater "strength" of the defects produced by irradiation, *viz.*, interstitials, vacancies, and foreign atoms.

The qualitative agreement between the calculations of Huang and the observed x-ray effects leads to the conclusion that the representation of localized static defects as elastic singularities producing displacements of the form $u=c/r^2$ is a valid first-approximation model. However, it is suggested that it may be possible to work back from the observed diffuse scattering in irradiated crystals to obtain more precise information regarding the distortions around the defects.

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Luminescent Centers in ZnS:Cu:Cl Phosphors

R. BOWERS AND N. T. MELAMED
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania
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Measurements of the magnetic susceptibility and emission spectra have been made on zinc sulfide activated by copper and/or chlorine. The results of these measurements demonstrate that the luminescent centers are diamagnetic in the absence of optical excitation, and that of the five previously reported emissions, only three are distinct. These are: a blue emission resulting from the addition of chloride, a green emission when copper and chloride are simultaneously present, and a red emission when copper alone is present. The results are discussed on an ionic model, and on a semiconductor model. We conclude that the blue emission is due to zinc vacancies, the green emission to substitutional copper, and the red emission to interstitial copper.

INTRODUCTION

IN this paper we shall attempt to correlate the reported emissions in ZnS activated by copper with particular states of the activator, especially the valence of the activator and its position in the lattice.

The absorption of a quantum of ultraviolet radiation by the host crystal of ZnS is usually assumed to result in the formation of an electron and a hole. These may annihilate one another by giving up their energy to the lattice as phonons, or they may recombine at an impurity center with a characteristic emission. The electronic transitions are governed by interactions between the impurity and the lattice; it is to be expected, therefore, that the resulting emission would depend on the state of ionization of the center. Furthermore, the energy levels may well depend on the crystallographic phase of the host crystal, and on whether the impurity is incorporated interstitially or substitutionally.

Information regarding the nature of impurity centers in impurity activated phosphors has been obtained for several manganese-activated inorganic phosphors by means of static susceptibility measurements,[1] and for a variety of phosphors by means of paramagnetic resonance.[2] In the case of ZnS:Cu, however, paramagnetic resonance measurements failed to yield any information because of the absence of an observable resonance absorption. The difficulties encountered in the resonance measurements, in being unable to distinguish between diamagnetism and a paramagnetism which results in a very broad absorption spectrum, are absent in the measurements of static susceptibility.

In the experiments to be described here, we have measured the emission spectra of a number of Cu-activated ZnS phosphors, prepared under various conditions, while at the same time, the phase has been determined from x-ray measurements. The state of ionization of the unexcited phosphors has been determined from measurements of the magnetic susceptibility as a function of temperature. Zinc sulfide is diamagnetic and, if the copper were introduced as Cu^+, it would remain purely diamagnetic and its susceptibility would be substantially independent of temperature. On the other hand, the presence of Cu^{++} or Cu^0

[1] S. Larach and J. Turkevich, Phys. Rev. **89**, 1060 (1953). P. D. Johnson and F. E. Williams, J. Chem. Phys. **17**, 435 (1949).

[2] W. D. Hershberger and H. N. Leifer, Phys. Rev. **88**, 714 (1952).

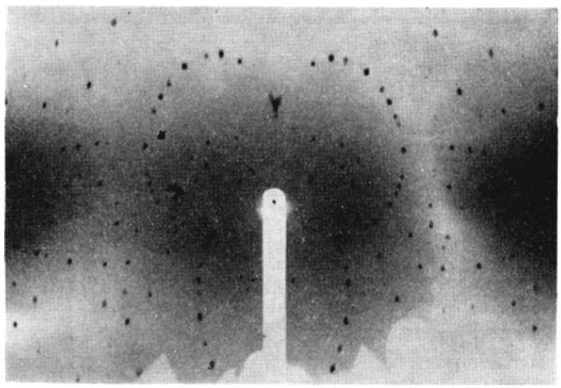

FIG. 1. Laue pattern of unirradiated diamond crystal using unfiltered copper x-radiation. Incident x-ray beam approximately parallel to threefold axis of crystal.

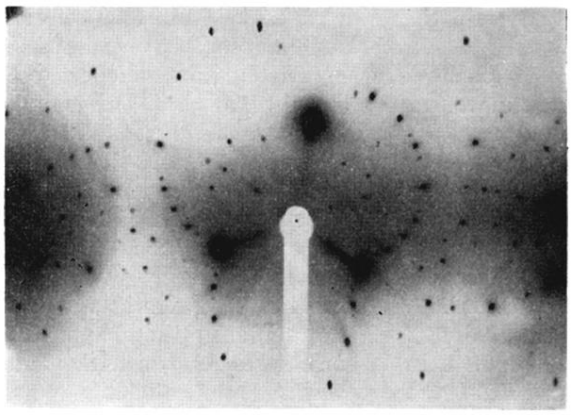

FIG. 2. Laue pattern of neutron irradiated diamond crystal using unfiltered copper x-radiation. Integrated thermal neutron flux 2×10^{20} neutrons/cm^2. Incident x-ray beam approximately parallel to threefold axis of crystal.