

per million by weight) for Harshaw were: Ca, 270; Fe, 100-1000; Al, 10-50; Cu, 10-100; Si, 5-10. Results for crystal C ("purest" Cornell grown crystal) were Ca, 400; Fe, <10; Al, 10-100; Cu, <2; Si, <50. The results of the calcium determinations were suspected to be incorrect, and they were repeated in an apparatus

especially designed to detect small amounts of Ca in the presence of alkali halides.³³ The results were 47 ppm for Harshaw and 50 ppm for crystal C. These lower figures are believed to be much more reliable.

³³ The measurements were performed by Q. Won Choi of the Cornell University Chemistry Department.

Magnetic Structure of Chromium Selenide*

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The magnetic structure of the NiAs-type compound, CrSe, has been determined by means of neutron diffraction. The indexing of superstructure lines which appear below the Néel point requires a unit cell three times as large as the conventional unit ($a = \sqrt{3}a_{\text{NiAs}}$). Planes parallel to the basal plane contain three chromium atoms whose spins form an "umbrella"-like array with threefold symmetry. Individual moments alternate in sign along lines parallel to the c axis. A value of $2.90 \mu_B$ has been deduced for the component of the chromium moment perpendicular to the c axis.

INTRODUCTION

A LARGE number of the sulfides, selenides, and tellurides as well as arsenides and antimonides of the transition metals have the nickel arsenide crystal structure. This structure, shown in Fig. 1, consists of a hexagonal close packing of the metalloid atoms with the transition metal atoms located in the interstices in such a way as to form a simple hexagonal array. The bond character as well as magnetic properties of these compounds and their solid solutions cover a rather wide spectrum. Some of the sulfides, such as CrS, are thought to be ionic, while the arsenides and antimonides, such as MnAs, are most probably covalent or metallic. Because of this range in bond character, the nature of the magnetic interaction can be expected to vary all the way from a direct (metallic-bond type) to an indirect (ionic bond) exchange mechanism. Some of the compounds,

e.g., CrS and MnTe, are antiferromagnetic while others, e.g., CrTe and MnAs, are ferromagnetic. The magnetic properties of these materials as well as solid solutions have been extensively investigated in recent years. In particular, the system¹ $\text{CrSe}_{1-x}\text{Te}_x$ has been examined and the pure compound CrSe was shown to have an anomalous temperature dependence of its susceptibility. The magnetic susceptibility data of Tsubokawa and of Lotgering and Gorter are shown in Fig. 2. The anomalies present in both sets of data below 300°K have led these authors to suggest a transition to an antiferromagnetic state. More recent measurements by Tsubokawa,² performed on single crystals of CrSe, indicate a Néel point close to 300°K and an effective moment of $4.90 \mu_B$, corresponding to a spin of 2 if the orbital moment is completely quenched. The paramagnetic moment reported by Lotgering and Gorter is approximately 10% lower than that given by Tsubokawa. A neutron

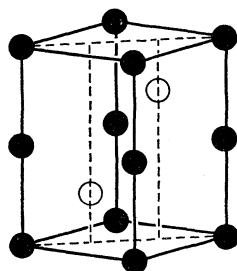


FIG. 1. Structure of CrSe.

● CHROMIUM
○ SELENIUM

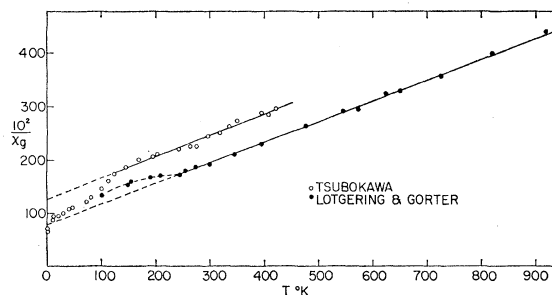


FIG. 2. Reciprocal susceptibility of CrSe as a function of temperature.

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¹ I. Tsubokawa, J. Phys. Soc. Japan **11**, 662 (1956); F. K. Lotgering and E. W. Gorter, J. Phys. Chem. Solids **3**, 238 (1957).

² K. Adachi (private communication).

diffraction investigation of CrSe was therefore undertaken to verify the existence of an antiferromagnetic transition and to determine the magnetic structure at low temperatures.

PREPARATION OF MATERIAL

The CrSe used in this investigation was prepared by the solid state reaction of purified chromium and selenium. Stoichiometric amounts of the two elements were intimately mixed and placed in a quartz tube. The tube was then heated to 250°C, evacuated, and placed in a furnace for 50 hr at a temperature of 950°C. This temperature is considerably below the melting point of CrSe which was found to be $1550 \pm 25^\circ\text{C}$. The reacted mixture was then slowly cooled to room temperature over a period of two days. An x-ray diffraction pattern of the reaction mixture was completely indexable on the basis of a simple hexagonal structure with the exception of a faint peak attributed to the chromium (110) reflection. This trace of chromium was not visible on the neutron diffraction pattern, indicating that it is concentrated on the surface of the crystallites and not present in the bulk of the material.

The unit cell dimensions of the CrSe, determined using Cu K_α radiation, are $a_0 = 3.674 \pm 0.004$ Å and $c_0 = 6.001 \pm 0.007$ Å. These measurements are in quite good agreement with those of Haraldsen and Mehmed.³

Several other samples of CrSe were prepared for which the composition of the starting material ranged from CrSe_{0.95} to CrSe_{1.05}. Samples were also quenched in water, rather than being slowly cooled from the reaction temperature. Neither of these changes in the method of preparation had any appreciable effect on the neutron diffraction pattern of CrSe.

NEUTRON DIFFRACTION DATA

Powder patterns were obtained at room temperature 77° and 4.2°K at a wavelength of 1.064 Å. The room temperature pattern was indexed on the basis of the nickel arsenide structure and was in good agreement with the calculated integrated intensities for this model.

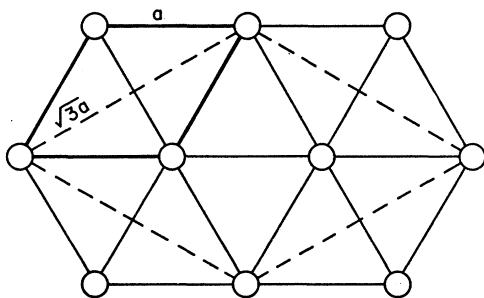


FIG. 3. Projection of the unit cell of CrSe on the basal plane. The chemical cell is shown in dark outline and the magnetic cell is indicated by the dashed lines.

³ H. Haraldsen and F. Mehmed, Z. anorg. u. allgem. Chem. **239**, 369 (1938).

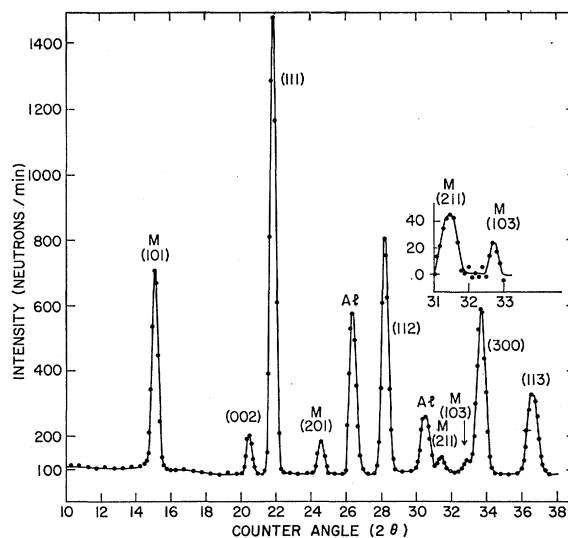


FIG. 4. Diffraction pattern of CrSe at 77°K. The indexing of lines is based upon the enlarged cell ($a = \sqrt{3}a_0$, $c = c_0$). Magnetic lines are indicated by the symbol M . The insert shows an enlargement of the region of the (211) and (103) magnetic peaks after graphical removal of the neighboring nuclear peaks.

The liquid-nitrogen as well as liquid-helium patterns showed a series of well-developed superstructure lines, indicating an antiferromagnetic transition somewhere between liquid nitrogen and room temperature. In order to index these magnetic superstructure lines, the unit cell must be enlarged as shown in Fig. 3. The new hexagonal unit cell has an a axis which is $\sqrt{3}$ times the original one, while the c axis remains unchanged. Hence, the volume of the magnetic unit cell is three times that of the chemical one. Figure 4 shows the neutron-diffraction pattern at liquid-nitrogen temperature. The hexagonal indexing shown on the pattern is based on the enlarged cell and the magnetic-superstructure lines have the symbol M attached. There is no change upon cooling to liquid helium.

ELIMINATION OF THE COLLINEAR MODEL

In order to explain the observed magnetic intensities, it would seem reasonable to first consider a collinear model, in which all spins are parallel and antiparallel to a fixed direction in the crystal. Unfortunately, this simple model fails, as can be seen from the following discussion. The three spins in the basal plane can have either the configuration $(+++)$ or $(++-)$ along the magnetic axis, with the spins at $z = \frac{1}{2}$ reversed in order to maintain zero net moment. The first choice $(+++)$ does not give rise to the observed superstructure reflections; indeed, this structure does not require the enlargement of the unit cell indicated by the indexing. The second arrangement does, however, give rise to the observed pattern, provided the spins are individually reversed in going from $z=0$ to $z=\frac{1}{2}$, producing antiferromagnetic chains in the c direction, and provided

also that the moment direction is taken parallel to the c axis. [The absence of $(00l)$ reflections with l odd, which would normally be present for this spin arrangement, requires that the magnetic axis coincide with the c axis in order to extinguish these reflections.] Intensities computed on the basis of this model and the required choice of magnetic axis are in serious disagreement with the observed intensities, as indicated in Table I.

NONCOLLINEAR SPIN ARRANGEMENTS

The failure of the collinear model leads us to a consideration of more general models in which the individual magnetic moments are no longer restricted to being parallel and antiparallel to a single direction in the crystal. The structure factor for a collection of spins having arbitrary orientations may be written as the complex vector quantity

$$\mathbf{F}_{hkl} = \sum p_i \mathbf{q}_i e^{2\pi i(hx_i + ky_i + lz_i)}, \quad (1)$$

where p_i is the magnitude of the scattering amplitude associated with the i th spin and \mathbf{q}_i is given by

$$\mathbf{q}_i = \mathbf{e}(\mathbf{e} \cdot \mathbf{k}_i) - \mathbf{k}_i, \quad (2)$$

in which \mathbf{e} is a unit vector parallel to the scattering vector and \mathbf{k}_i is a unit vector parallel to the magnetic moment. Defining the quantity \mathbf{K}_{hkl} by the expression

$$\mathbf{K}_{hkl} = \sum \mathbf{k}_i e^{2\pi i(hx_i + ky_i + lz_i)}, \quad (3)$$

the structure factor can be written in the form

$$\mathbf{F}_{hkl} = \mathbf{e}(\mathbf{e} \cdot \mathbf{K}_{hkl}) - \mathbf{K}_{hkl}, \quad (4)$$

in which the p_i have, for convenience, been taken equal to unity. The intensity of a powder-diffraction line is proportional to the square of \mathbf{F} averaged over all members of the crystallographic form. Thus,

$$\langle \mathbf{F} \cdot \mathbf{F}^* \rangle = \langle \mathbf{K} \cdot \mathbf{K}^* \rangle - \langle (\mathbf{e} \cdot \mathbf{K})(\mathbf{e} \cdot \mathbf{K}^*) \rangle. \quad (5)$$

"UMBRELLA" MODEL

Let us now consider the case of a hexagonal crystal with atoms in the special positions

$$\begin{aligned} & \frac{1}{3}, 0, 0; \quad 0, \frac{1}{3}, 0; \quad \frac{2}{3}, \frac{2}{3}, 0 \\ & \frac{1}{3}, 0, \frac{1}{2}; \quad 0, \frac{1}{3}, \frac{1}{2}; \quad \frac{2}{3}, \frac{2}{3}, \frac{1}{2}, \end{aligned}$$

and possessing magnetic moments oriented so as to retain at least threefold symmetry. The most general configuration of spins is that of an "umbrella" as shown in Fig. 5. In the following discussion, the angles between any one spin and the cell axes are taken to be arbitrary.

The vectors \mathbf{K}_{hkl} of Eq. (3) for three symmetry-related reflections, are

$$\begin{aligned} \mathbf{K}_{hkl} = & (\mathbf{k}_1 + \mathbf{k}_4 e^{\pi i l}) e^{2\pi i h/3} + (\mathbf{k}_2 + \mathbf{k}_5 e^{\pi i l}) e^{2\pi i k/3} \\ & + (\mathbf{k}_3 + \mathbf{k}_6 e^{\pi i l}) e^{-2\pi i (h+k)/3}, \end{aligned} \quad (6)$$

$$\mathbf{K}_{-h-k, h, l} = \mathbf{K}_{hkl} e^{2\pi i (h-k)/3},$$

$$\mathbf{K}_{l, -h-k, l} = \mathbf{K}_{hkl} e^{-2\pi i (h-k)/3},$$

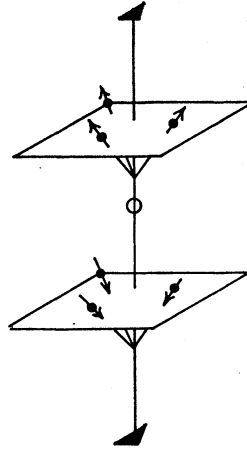


FIG. 5. "Umbrella" model for spin configuration in CrSe. The magnetic moments in both the $z=0$ and $z=\frac{1}{2}$ level of the unit cell are shown in relation to the threefold axis.

in which $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$ are the spin vectors at $z=0$ and $\mathbf{k}_4, \mathbf{k}_5, \mathbf{k}_6$ are the corresponding vectors at $z=\frac{1}{2}$.

If the vectors \mathbf{e} and \mathbf{K} are referred to a set of orthogonal axes with x and y in the basal plane and z along the c axis, we have, for a given reflection hkl ,

$$\begin{aligned} (\mathbf{e} \cdot \mathbf{K})(\mathbf{e} \cdot \mathbf{K}^*) &= e_x^2 K_x K_x^* + e_y^2 K_y K_y^* + e_z^2 K_z K_z^* \\ &+ e_x e_y (K_x K_y^* + K_x^* K_y) + e_y e_z (K_y K_z^* + K_y^* K_z) \\ &+ e_x e_z (K_x K_z^* + K_x^* K_z). \end{aligned}$$

The coefficients of $e_x^2, \dots, e_x e_z$ are invariant for the three symmetry-related reflections by virtue of relations (6) and hence,

$$\begin{aligned} \langle (\mathbf{e} \cdot \mathbf{K})(\mathbf{e} \cdot \mathbf{K}^*) \rangle &= \langle e_x^2 \rangle K_x K_x^* + \langle e_y^2 \rangle K_y K_y^* + \langle e_z^2 \rangle K_z K_z^* \\ &+ \langle e_x e_y \rangle (K_x K_y^* + K_x^* K_y) + \langle e_y e_z \rangle (K_y K_z^* + K_y^* K_z) \\ &+ \langle e_x e_z \rangle (K_x K_z^* + K_x^* K_z). \end{aligned}$$

Furthermore, noting that

$$e_x = (1 - e_z^2)^{1/2} \cos \phi, \quad e_y = (1 - e_z^2)^{1/2} \sin \phi,$$

where ϕ is the angle between the projection of the normal on the basal plane and the x axis, we have, after averaging over the three reflections,

$$\langle e_x^2 \rangle = \langle e_y^2 \rangle = \frac{1}{2}(1 - e_z^2) \quad \text{and} \quad \langle e_x e_y \rangle = \langle e_y e_z \rangle = \langle e_x e_z \rangle = 0.$$

Thus,

$$\langle (\mathbf{e} \cdot \mathbf{K})(\mathbf{e} \cdot \mathbf{K}^*) \rangle = \frac{1}{2}(1 - e_z^2)(\mathbf{K} \cdot \mathbf{K}^*) + \frac{1}{2}(3e_z^2 - 1)K_z K_z^*,$$

and,

$$\langle \mathbf{F} \cdot \mathbf{F}^* \rangle = \frac{1}{2}(1 + e_z^2)(\mathbf{K} \cdot \mathbf{K}^*) + \frac{1}{2}(1 - 3e_z^2)K_z K_z^*, \quad (7)$$

where

$$\begin{aligned} \mathbf{K} \cdot \mathbf{K}^* = & k_a^2 + k_b^2 + k_c^2 + 2 \cos \left[\frac{2}{3} \pi (2h + k) \right] \\ & \times \{ \mathbf{k}_a \cdot \mathbf{k}_b + \mathbf{k}_b \cdot \mathbf{k}_c + \mathbf{k}_a \cdot \mathbf{k}_c \}, \end{aligned}$$

and

$$\begin{aligned} K_z K_z^* = & k_{az}^2 + k_{bz}^2 + k_{cz}^2 + 2 \cos \left[\frac{2}{3} \pi (2h + k) \right] \\ & \times \{ k_{az} k_{bz} + k_{bz} k_{cz} + k_{az} k_{cz} \}, \end{aligned} \quad (8)$$

in which $\mathbf{k}_a = \mathbf{k}_1 \pm \mathbf{k}_4$, $\mathbf{k}_b = \mathbf{k}_2 \pm \mathbf{k}_5$, $\mathbf{k}_c = \mathbf{k}_3 \pm \mathbf{k}_6$, the upper and lower signs corresponding to l even or odd.

Equations (7) and (8) have been derived for three reflections related by a threefold axis, but apply equally well to the whole crystallographic form.

APPLICATION TO CrSe

Equation (7) can be simplified by making use of the fact that the (100) reflection is absent. For $l=0$, $\mathbf{k}_a = \mathbf{k}_1 + \mathbf{k}_4$, $\mathbf{k}_b = \mathbf{k}_2 + \mathbf{k}_5$, and $\mathbf{k}_c = \mathbf{k}_3 + \mathbf{k}_6$. In addition, the sum of all the moments, $\mathbf{k}_a + \mathbf{k}_b + \mathbf{k}_c$, must vanish by virtue of the antiferromagnetic condition. Thus, using (8), $(\mathbf{K} \cdot \mathbf{K}^*)_{100} = \frac{3}{2}(k_a^2 + k_b^2 + k_c^2)$. Furthermore, since by symmetry, the z components of spins 1, 2, 3 are equal and opposite to those of 4, 5, 6, we have $k_{az} = k_{bz} = k_{cz} = 0$ and $(K_z K_z^*)_{100} = 0$. Equation (7) now reduces to the expression $\langle (\mathbf{F} \cdot \mathbf{F}^*) \rangle_{100} = \frac{3}{4}(k_a^2 + k_b^2 + k_c^2) = 0$, and hence, $\mathbf{k}_a = \mathbf{k}_b = \mathbf{k}_c = 0$; i.e., $\mathbf{k}_1 = -\mathbf{k}_4$, $\mathbf{k}_2 = -\mathbf{k}_5$, $\mathbf{k}_3 = -\mathbf{k}_6$. We then see that the absence of the (100) reflection imposes the condition that *the spins alternate along a line parallel to the c axis*. It should be noted that this conclusion is not obvious from either symmetry or the antiferromagnetic nature of the crystal, since it would be possible to satisfy both requirements by permitting the spins at $z=0$ and $z=\frac{1}{2}$ to have the same x and y components.

Substituting this result into Eq. (8), we obtain for l odd

$$\begin{aligned} \mathbf{K} \cdot \mathbf{K}^* &= 12\{1 + 2\mathbf{k}_i \cdot \mathbf{k}_j \cos[\frac{2}{3}\pi(2h+k)]\}, \\ K_z K_z^* &= 12k_z^2\{1 + 2\cos[\frac{2}{3}\pi(2h+k)]\}, \end{aligned}$$

where i and j refer to any single pair of spins 1, 2, and 3, and k_z is the z component of an individual spin. If θ is the angle between the c axis and any one spin vector, the scalar product $\mathbf{k}_i \cdot \mathbf{k}_j$ can, because of the threefold symmetry, be replaced by the expression $\frac{1}{2}(3\cos^2\theta - 1)$. Making this substitution and reinserting the magnitude of the magnetic scattering amplitude ($p=0.27\mu$), we obtain, after some reduction, the following expressions for the mean-square structure factors corresponding to the various classes of reflections:

$$\begin{aligned} \langle (\mathbf{F} \cdot \mathbf{F}^*) \rangle &= 0 \quad \text{for } l \text{ even;} \\ \langle (\mathbf{F} \cdot \mathbf{F}^*) \rangle &= 0.654 \mu_1^2 (1 + e_z^2) \\ &\quad \text{for } l \text{ odd, } 2h+k=3n\pm 1; \\ \langle (\mathbf{F} \cdot \mathbf{F}^*) \rangle &= 2.61 \mu_1^2 (1 - e_z^2) \quad \text{for } l \text{ odd, } 2h+k=3n. \end{aligned} \quad (9)$$

In these expressions, $\mu_1 = \mu \sin\theta$ and $\mu_{11} = \mu \cos\theta$ are the components of the individual spins perpendicular and parallel to the c axis and e_z is the z component of the normal to any member of a given set of equivalent planes. The quantities $\langle (\mathbf{F} \cdot \mathbf{F}^*) \rangle$ must of course be multiplied by the multiplicity of the form in computing the actual intensity of a powder reflection.

COMPARISON WITH EXPERIMENT

Reflections with l odd and $2h+k=3n\pm 1$ are purely magnetic in origin, whereas those with $2h+k=3n$ are

TABLE I. Comparison of observed and calculated intensities.

hkl	I_{calc}		I_{obs}
	Collinear model	"Umbrella" model	
101	1858	1858	1858
201	639	337	342
211	514	235	216
103	26	160	164
	$\mu = 3.57 \mu_B^a$	$\mu_1 = 2.90 \mu_B^a$	

^a Computed by normalization of magnetic intensities relative to the nuclear intensities.

mainly nuclear. In principle, it would be possible, with the aid of Eqs. (9) to determine both the magnitude of the magnetic moment and the angle of inclination of the spin with respect to the hexagonal axis. In practice, however, since the magnetic contributions to the $2h+k=3n$ peaks are only a few percent of the total, and since small deviations from ideal stoichiometry and order may conceivably affect the calculation of the nuclear contributions to be subtracted, one cannot calculate μ_{11} with appreciable reliability. Furthermore, a qualitative examination of the temperature dependence of the purely magnetic reflections shows no sharp transition temperature but rather a gradual decrease in magnetic intensity from approximately 100°K to room temperature. This behavior prevents an accurate subtraction of the nuclear contributions to the $2h+k=3n$ peaks by comparing intensities above and below the Néel point.

It is nevertheless possible to test the validity of the "umbrella" model by comparing the relative intensities of the purely magnetic reflections ($2h+k=3n\pm 1$), inasmuch as they depend only on the angle between the normal to the reflecting plane and the hexagonal axis. Inspection of Table I indicates that excellent agreement between calculated and observed intensities is obtained with the model. Normalization of the magnetic intensities, by comparison with the nuclear reflections, yields a value of $2.90 \mu_B$ for the component of the magnetic moment perpendicular to the hexagonal axis. For a total moment close to the theoretical "spin-only" value of $4 \mu_B$, the angle of inclination of the spin to the c axis corresponds to approximately 45°. Calculated intensities for the collinear model are also given in Table I. It can be seen immediately from the table that the collinear model is unsatisfactory.

DISCUSSION

CrSe represents an unambiguous example of a non-collinear antiferromagnetic spin arrangement. Angular arrangements of spins have been assumed by Yafet and Kittel⁴ and Lotgering⁵ to explain the magnetic properties of ferrites as well as some oxides and sulfides, but heretofore clear-cut experimental evidence for the existence of such arrangements has been lacking. After the

⁴ Y. Yafet and C. Kittel, Phys. Rev. **87**, 290 (1952).

⁵ F. K. Lotgering, Philips Research Repts. **11**, 190, 337 (1956).

experimental determination of the structure, our attention was drawn to the work of Hirone and Adachi⁶ who considered the magnetic properties of the NiAs structures in the molecular-field approximation. They showed that triangular spin configurations were stable over certain regions of the molecular-field coefficients of first, second, and third nearest neighbors. Indeed, the ordering in CrSe corresponds to a generalized form of their ordering of the third kind if the spins are tilted out of the basal plane, and corresponds exactly with it if μ_{11} is zero.

The noncollinear spin arrangement would also be expected to influence the susceptibility below the Néel temperature and may conceivably account for the anomalous behavior.

It is perhaps interesting to examine the possible mag-

⁶ T. Hirone and K. Adachi, J. Phys. Soc. Japan **12**, 156 (1957).

netic space groups which allow the proposed model; these include both ordinary as well as Shubnikov groups.⁷ $P\bar{6}2m$ and $P\bar{6}2'm'$, where the primes indicate antielements, restrict the Cr moment to the basal plane perpendicular and parallel to the unit-cell edges, respectively. $P321$ and $P31m'$ correspond to the more general cases in which the Cr moment has both a perpendicular and parallel component with respect to the c axis. The last group $P3$ permits the moments to have an arbitrary direction, simply maintaining threefold symmetry. It is seen that an independent determination of the space group below the transition could enable one to restrict the possible structures.

⁷ N. V. Belov, N. N. Neronova, and T. S. Smirnova, *Kristallografiya* **2**, 315 (1957); G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliott, and J. M. Hastings, *Phys. Rev.* **112**, 1917 (1958).

Mechanism for Production of Interstitials in KCl by X Rays at Low Temperatures

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Experimental evidence indicates that halogen vacancies and interstitials may be formed by x irradiation of KCl at low temperatures. The validity of a mechanism based on multiple ionization depends upon several factors; among them efficiency of ionization and the availability of sufficient kinetic energy to remove the interstitial from the immediate vicinity of the vacancy. These two conditions are considered in some detail and found to be satisfied.

1. INTRODUCTION

OF the several mechanisms that have been suggested for the production of defects in alkali halides by ionizing radiation, the Varley mechanism¹ (and its modifications) is the only one that (1) accounts for the production of interstitial halogen ions and (2) describes the defect production in terms of bulk properties of the crystal rather than in terms of dislocations or impurities.²⁻⁴ It is consistent therefore with evidence for the ex-

istence of interstitials^{5,6} and also with recent experiments that strongly suggest that production of F centers at liquid He temperature depends only on bulk properties.⁷ According to Varley, a certain number of halogen ions become multiply ionized by the absorbed radiation. These ions are positively charged with respect to the lattice. Hence, a small perturbation, either by lattice vibrations or by other means, may be sufficient to eject a multiply ionized halogen from a normal lattice site to an electrostatically more favorable interstitial position. The vacancy left behind would capture an electron to become an F center. One of the objections to this process is that the ejected ion is very close to the vacancy and prompt recombination is likely. Also, the

* A large part of the work here reported was done when the authors were at the Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

¹ J. H. O. Varley, *Nature* **174**, 886 (1954) and *J. Nuclear Energy* **1**, 130 (1954).

² F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

³ J. H. Crawford, Jr. and C. M. Nelson, *Phys. Rev. Letters* **5**, 314 (1960).

⁴ P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **121**, 484 (1961) and P. V. Mitchell, Ph.D. Thesis, Carnegie Institute of Technology (1960).

⁵ W. Kaenzig and T. O. Woodruff, *Phys. Rev.* **109**, 220 (1958), and private communication.

⁶ D. A. Wiegand and R. Smoluchowski, *Phys. Rev.* **110**, 991 (1958).

⁷ H. Rabin and C. C. Klick, *Phys. Rev.* **117**, 1005 (1960).