Picus, and Henvis[3] have informed us of results of infrared absorption measurements on arsenic- and phosphorus-doped silicon. We should like to suggest an interpretation of their absorption lines leading to very good agreement with our theoretical results, which have since been supplemented by calculations of the $(3p, m=\pm1)$ level and of oscillator strengths, as well as by a more refined calculation of the $(2p, m=0)$ level, which in reference 1 had a slightly larger uncertainty.

Theoretical results for the lowest four excited states to which optical transitions take place at all appreciably are listed in Table I. The quoted intensities are for arsenic donors and have an uncertainty of perhaps ±30 percent (phosphorus donors give slightly different values.)

TABLE I. Optically excited donor states; theory.

States	Energy below continuum (in units of 0.01 ev)	Intensity of transition from 1*s* ground state (arbitrary scale)
$2p, m=0$	-1.09 ± 0.02	4.0
$2p, m=+1$ and -1	-0.59 ± 0.01	10.6
$3p, m=0$	-0.57 ± 0.06	0.4
$3p, m=+1$ and -1	-0.29 ± 0.005	3.1
$4p, f, m=+1$ and -1	No detailed results	No detailed results

It will be seen that the $(1s)-(3p, m=0)$ transition is quite likely to escape detection in view of its small intensity and the proximity of the latter level to the $(2p, m=\pm1)$ level (see Table I). The lowest three observed transitions I, II, III should then be associated with the $(2p, m=0)$, $(2p, m=\pm1)$ and $(3p, m=\pm1)$ levels. The fourth observed transition, IV, is very likely to be associated with the $(4p, f, m=\pm1)$ level but no detailed theoretical results are available.

Table II contains the experimental results with the suggested interpretation and Table III compares the spacings between the observed lines with the corresponding theoretical spacings. The agreement between theory and experiment is very satisfactory.[4]

TABLE II. Observed infrared absorption lines.[a]

Observed line	Energy above the ground state (in units of 0.01 ev) As-donors	P-donors
I: $(1s)\rightarrow(2p, m=0)$	4.23	3.44
II: $(1s)\rightarrow(2p, m=\pm1)$	4.72[b]	3.97
III: $(1s)\rightarrow(3p, m=\pm1)$	5.06	
IV: $(1s)\rightarrow(4p, f, m=\pm1)$	5.21	

[a] These were kindly communicated to us by Dr. Picus and are more accurate than those mentioned in reference 2.

[b] E. Burstein *et al.*, find consistently a small secondary peak on this line which may be associated with the $3p$, $m=0$ level (see Table I).

By combining the experimental energy differences between the excited states and the ground state with the theoretical positions of the excited states, relative to the continuum, we obtain the following ionization energies of the ground states. As: 0.0533 ± 0.0003 ev; P: 0.0455 ± 0.0003 ev.

TABLE III. Spacings of excited states.

States	Energy difference (in units of 0.01 ev) Theory	Observed
$(2p, m=\pm1)$ $-(2p, m=0)$	0.50 ± 0.02	0.49 (As) 0.53 (P)
$(3p, m=\pm1)$ $-(2p, m=\pm1)$	0.30 ± 0.01	0.34 (As)
$(4p, f, m=\pm1)$ $-(3p, m=\pm1)$	No detailed results	0.15 (As)

The agreement between theory and experiment, which has been described, constitutes a verification of the consistency of the effective mass formalism: The same effective masses which govern cyclotron resonances also determine quite accurately the positions of the impurity states of "*p*"-symmetry, as had been theoretically anticipated.[5]

A detailed report is in preparation.

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[1] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 1721 (1955); see also Phys. Rev. **98**, 1561(A) (1955).

[2] W. H. Kleiner, Phys. Rev. **97**, 1722 (1955). I am indebted to Dr. Kleiner for sending me a copy of his paper before publication.

[3] I am grateful to these authors for acquainting me with their results, obtained with Bell Telephone Laboratories specimens, which will shortly be published.

[4] W. H. Kleiner, reference 2, has associated the lowest four transitions with the $(2p, m=0)$, $(2p, m=\pm1)$, $(3p, m=0)$, and $(3p, m=\pm1)$ levels. By not omitting the $(3p, m=0)$ level he finds poor agreement between theory and experiment.

[5] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955). The position of the ground state is not well described by the theory (which predicts -0.029 ev for all donors) because it penetrates into the imperfectly understood region near the donor nucleus.

New Method in X-Ray Crystal Structure Determination Involving the Use of Anomalous Dispersion

Y. OKAYA, Y. SAITO,[*] AND R. PEPINSKY

X-Ray and Crystal Structure Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania

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WHEN incident x-rays strike a crystal, and the wavelength of the x-rays is just shorter than a resonance level of a particular atom in the crystal, the radiation is scattered with abnormal phase and amplitude. In such a case, Friedel's rule does not hold, and $|F_{hkl}| \neq |F_{\bar{h}\bar{k}\bar{l}}|$. Excellent use of this phenomenon has been made in determinations of absolute configurations of structures which may exist in enantiomorphous arrangements.[1] The technique employed heretofore has involved determination of the structure except for choice between enantiomorphous forms, without anomalous scattering, and then utilization of the influence of anomalous dispersion upon a limited number of structure factors to decide on the absolute configuration.

The present analysis concerns a direct procedure for obtaining information concerning the structure and absolute configuration of a noncentrosymmetric crystal containing anomalously scattering atoms.

The structure factor F_{hkl} can be written as

$$\begin{aligned} F_{hkl} &= \sum_j f_j \exp[2\pi i(hx_j+ky_j+lz_j)] \\ &= \sum_j f_j \exp[i\theta_j(hkl)], \end{aligned} \tag{1}$$

where

$$\theta_j(hkl) = 2\pi(hx_j+ky_j+lz_j). \tag{2}$$

For normal scattering, the atomic scattering factors f_j are real. In the case of anomalous scattering, however,

$$f_j = f_j' + if_j''. \tag{3}$$

It can be shown readily, then, that

$$\begin{aligned} F_{hkl}^2 = \sum_{j,i} (f_j'f_i'+f_j''f_i'') \cos 2\pi[h(x_j-x_i)+k(y_j-y_i) \\ +l(z_j-z_i)] + \sum_{j,i} (f_j'f_i''-f_j''f_i') \\ \times \sin 2\pi[h(x_j-x_i)+k(y_j-y_i)+l(z_j-z_i)], \end{aligned} \tag{4}$$

the summation being extended over all pairs of j and i.

We now construct two Patterson series, using F_{hkl}^2 as coefficients:

$$P_c(u,v,w) = \sum_{\substack{hkl \\ -\infty}}^{\infty} F_{hkl}^2 \cos 2\pi(hu+kv+lw), \tag{5}$$

$$P_s(u,v,w) = \sum_{\substack{hkl \\ -\infty}}^{\infty} |F_{hkl}|^2 \sin 2\pi(hu+kv+lw). \tag{6}$$

The even function $P_c(u,v,w)$ contains peaks of heights equal to $f_j'f_i'+f_j''f_i''$ at the points $\pm(u,v,w) = \pm[(x_j-x_i)(y_j-y_i)(z_j-z_i)]$; the odd function $P_s(u,v,w)$ shows peaks of height $f_j'f_i''-f_j''f_i'$ at the points (u,v,w), together with peaks of height $-(f_j'f_i''-f_j''f_i')$ at $(-u, -v, -w)$. $P_c(u,v,w)$ and $P_s(u,v,w)$ represent the real and the imaginary parts respectively of the convolution of the distribution of scattering power in the unit cell.

If the jth and the ith atoms are of the same kind, the peaks at $\pm[(x_j-x_i)(y_j-y_i)(z_j-z_i)]$ in $P_s(u,v,w)$ disappear. Thus P_s indicates only interactions between different kinds of atoms. If only one atom, say the mth, scatters x-rays with anomalous phase and amplitudes, we have

$$\begin{aligned} f_j' &= f_j,\ f_j''=0 \quad (j\neq m), \\ f_j'' &\neq 0 \quad (j=m). \end{aligned}$$

Then $P_s(u,v,w)$ has peaks of height f_jf_m'' at $[(x_j-x_m), (y_j-y_m), (z_j-z_m)]$ and $-f_jf_m''$ at $[(x_m-x_j), (y_m-y_j), (z_m-z_j)]$. Since the peaks at $[(x_j-x_m)(y_j-y_m)(z_j-z_m)]$ and $[(x_m-x_j)(y_m-y_j)(z_m-z_j)]$ are positive and negative respectively, we can distinguish between them; hence we can specify the *magnitude* and *direction* (including the *sense*) of the vector between the mth and jth atoms.

The only limitations to the determinations of these vectors will arise from accidental superposition of positive and negative peaks, due to pseudocentric symmetry in disposition of some atoms about an anomalous scatterer. This overlapping can be reduced by suitable sharpening of the scattering factors, through the use of standard techniques.

Both a Patterson function without anomalous scattering, and P_c in the case of anomalous scattering, contain $N(N-1)$ peaks for N atoms in the cells. P_s contains only $2n(N-n)$ peaks, where n is the number of anomalously scattering atoms per cell. Half of these latter peaks are positive, and half negative; and all result from interactions between anomalous scatterers and normally scattering atoms only. One immediate advantage of this is the possibility of selection of nonrotational vectors for use in image-seeking methods of Patterson map deconvolution.[2]

When the number of anomalously scattering atoms is small, the advantages of the use of P_s in a complete noncentrosymmetric structure determination, and not merely for the establishment of absolute configuration, are obvious. With but one anomalous scatterer per asymmetric unit of a cell, an absolute-configuration analysis is possible directly in three dimensions. Methods for the "engineering" of crystals of optically active organic molecules with desirable symmetries and suitable anomalous scatterers have been discussed recently by one of us (R.P.).[3] If crystals with amenable distributions of anomalous scatterers *can* be prepared, and sufficient care can be taken to obtain accurate scattered intensity information, the phase problem for moderately complex noncentric structures can be greatly alleviated if not fully solved.

The method has been successfully applied in a direct determination of the structure and absolute configuration of $[d-\mathrm{Co}(en)_3]\mathrm{Cl}_3 \cdot \mathrm{NaCl} \cdot 6\mathrm{H}_2\mathrm{O}$. The structure and absolute configuration of this crystal were previously determined, via the standard anomalous dispersion method, by Saito *et al.*[4] The above example of the new method will be published elsewhere.

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[*] On leave from Department of Chemistry, Osaka City University, Osaka, Japan.

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