

Is Potassium Chlorate a Ferroelastic?

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Abstract

New twin domains of thickness of the order of a few micrometres can be created in KClO_3 crystals by applying a small uniaxial stress. The observed domain structure can be explained by postulating a hypothetical prototype phase of symmetry $4/mmm$. The magnitude of spontaneous strain, σ_s , for the room-temperature monoclinic phase, computed on the basis of the postulated tetragonal prototype, has an exceptionally large value of 0.257. Further, σ_s varies linearly as the square root of temperature, implying a mean-field-like behaviour. However, presumably because of the very large spontaneous strain, attempts to move the domain walls back and forth by applying uniaxial stress (at room temperature) have not yet been successful, and the question asked in the title may be a matter of definition.

1. Introduction

Potassium chlorate crystals have attracted the attention of a large number of workers for nearly a hundred years, particularly because of their beautiful pearly lustre and iridescence. Ramachandran & Lonappan (1957) have briefly reviewed the earlier studies. The crystals are monoclinic pseudo-orthorhombic at room temperature. From aqueous solution they frequently grow as rhombus-shaped, multiply-twinned c plates (b axis unique). The twin planes in such crystals are typically about $1 \mu\text{m}$ apart, and are parallel to the large c face. The pearly lustre arises from multiple reflection of light by these twin planes. Iridescence is believed to occur in only those crystals in which all the twin components are of the same thickness, so that interference effects, apart from birefringence and some other effects, can take place (Rayleigh, 1889; Raman & Krishnamurti, 1953).

The above type of twinning appears to be the only type investigated in these crystals. In this paper we report the creation of this as well as some other,

hitherto unreported, types of twin planes by the application of uniaxial stress. We believe that this implies that the crystals can be called ferroelastic, although some workers may prefer not to consider the evidence as sufficient. This point is discussed further in § 2.

Room-temperature X-ray diffraction studies of the crystal structure of KClO_3 were carried out by Zachariassen (1929), Arvindakshan (1958) and Bats (1978). The crystals belong to the space group $P2_1/m$, with $Z = 2$, and have the following lattice parameters (Zachariassen, 1929): $a_0 = 4.647$, $b_0 = 5.585$, $c_0 = 7.085 \text{ \AA}$, $\beta = 109.63^\circ$. The pseudo-orthorhombic character of the lattice is made explicit by the following cell transformation (Fig. 1a), which gives a cell with $Z = 4$:

$$\mathbf{a} = \mathbf{a}_0; \quad \mathbf{b} = \mathbf{b}_0; \quad \mathbf{c} = 2\mathbf{c}_0 + \mathbf{a}_0. \quad (1)$$

The new lattice parameters are: $a = 4.647$, $b = 5.585$, $c = 13.347 \text{ \AA}$, $\beta = 90.49^\circ$.

The crystals transform to an orthorhombic phase of symmetry $Pcmm$ at a temperature reported in the literature as 523 K (Ramachandran & Lonappan, 1957; Pistorius, 1970). This is a first-order anti-ferrodistortive phase transition, involving cell doubling along the c direction (Fig. 1a).

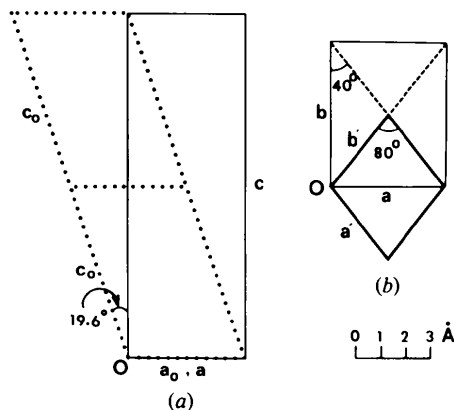


Fig. 1. (a) Cell transformation corresponding to equations (1). (b) Relationship between the room-temperature lattice vectors \mathbf{a} and \mathbf{b} and the postulated prototype-phase lattice vectors \mathbf{a}' and \mathbf{b}' [equations (2)]. The third lattice vector, \mathbf{c}' , is along \mathbf{c}_0 ($\mathbf{c}' = 2\mathbf{c}_0$).

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2. Stress-induced domain structure of KClO_3 and the question of defining ferroelastics

Fig. 2 shows the effect of applying a small stress along the length of a needle-shaped crystal of KClO_3 . The twin planes (domain walls) shown in these photographs are the type which occur in some as-grown c plates also, and are the ones responsible for their pearly lustre or iridescence. Their creation under stress was also mentioned by Madan (1886). However, some other types of domain walls can also be created by applying a small uniaxial stress. Fig. 3 shows these. For convenience in further discussion, we designate the various types of observed domain walls in the monoclinic phase of KClO_3 as follows (they are also shown in stereographic projection in Fig. 4).

DW1: Domain walls parallel to the c face. These can be seen almost edge on in Fig. 2.

DW2: Domain walls containing the b axis and inclined from the normal to the c face by 21° (Fig. 3).

DW3: Domain walls whose intersection line with the c face makes an angle of 40° with the b axis, and which are inclined to the c -face normal by 17° (Fig. 3).

DW4: Similar to DW3, except that the angle between the intersection line with the c face and the b axis is -40 instead of 40° (Fig. 3).

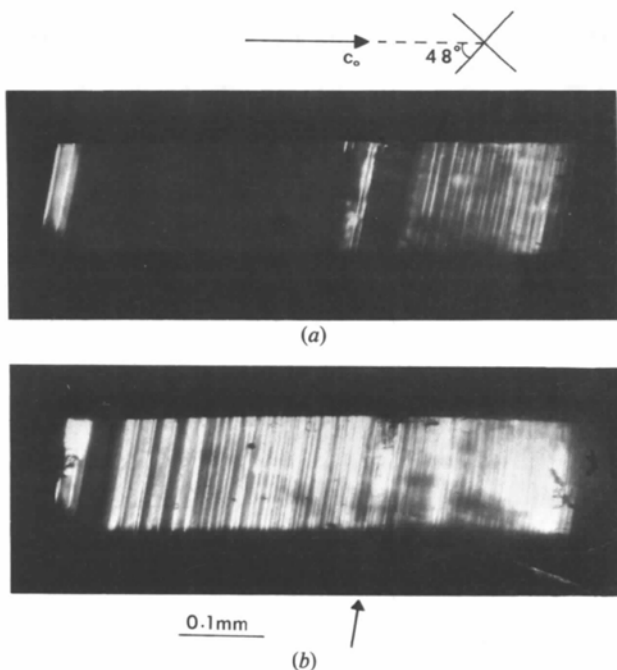


Fig. 2. Polarizing-microscope photographs of a needle-shaped crystal of KClO_3 elongated along c_0 . The crystal shown in (a) changed to that in (b) when it was pressed lightly along the needle axis. The cross indicates the orientation of the crossed polars. The domain walls seen in (a) and (b) (and designated DW1) are also planes of easy cleavage; the arrow at the bottom of (b) shows the spot where cleavage developed on further pressing.

Is KClO_3 ferroelastic at room temperature? There are two approaches to the question of defining ferroics in general, and ferroelastics in particular (Aizu, 1970a). The first emphasizes the requirement of state shifts (domain switching) between the orientation states, and the second is based on (real or hypothetical) ferroic phase transitions. The first approach (Abrahams, 1971) requires not only the switchability of the ferroelastic domains, but also the *reproducibility* of the switching; it is implied by Abrahams' (1971) definition that it should be possible not only to *create* new domains in a ferroelastic, but also to *eliminate* existing ones by changing them to another orientation state. The phase-transitions approach for defining ferroics (Aizu,

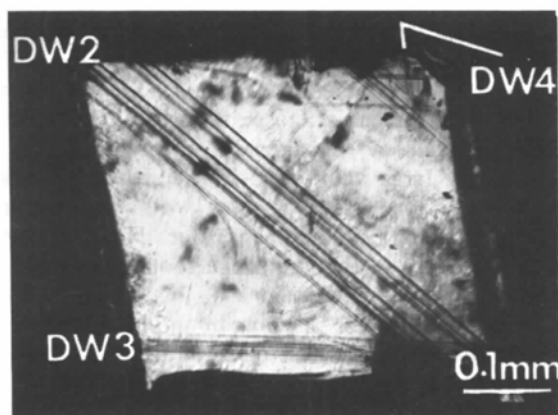


Fig. 3. A c plate of KClO_3 , showing new types of domain walls created by applying uniaxial stress. Three types of walls could be thus created, apart from DW1 seen in Fig. 2. These are labelled DW2, DW3 and DW4 (see § 2 of the text). The crossed polars were set at 45° to the b axis, which is along the long diagonal of the rhombus-shaped crystal.

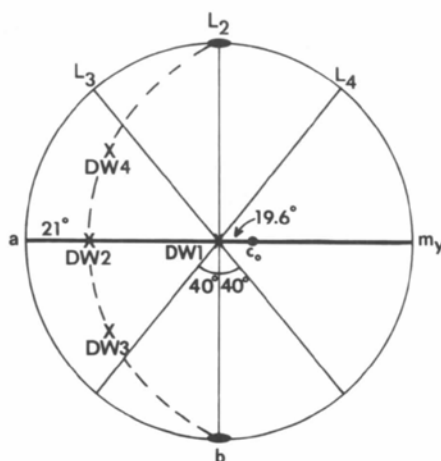


Fig. 4. Stereographic projection along c , showing the orientations of the various domain walls. The crosses indicate the projections of the normals to the domain walls. L_2 , L_3 and L_4 are the lines of intersection of DW2, DW3 and DW4 with the c face. Notice that DW2, DW3 and DW4 have a common zone axis, approximately along c_0 .

1970a; Janovec, Dvořák & Petzelt, 1975) is a more general one, and enables one to apply the formalism developed for classifying ferroics to the majority of structural phase transitions. Any phase transition in a crystal that entails a change of point-group symmetry is, in general, a potentially ferroic transition because it will inevitably lead to the possibility of equivalent orientation states, and hence domain structure. (The statement can be generalized to changes of space-group symmetry also.) Whether the domain walls can be moved or not (by applying a suitable coercive force) is a question of secondary importance only. Since the contribution to the free energy from the term(s) responsible for ferroic behaviour tends to zero as the temperature for transition to the prototype phase is approached, domain-switching can, in principle, be always achieved by applying the coercive force at a temperature close enough to the transition temperature.

If one adopts the definition of Abrahams (1971), KClO_3 cannot yet be called a ferroelastic because, although new domains *can* be created in it by applying a compressive stress (Figs. 2 and 3), it has not yet been possible to demonstrate the *back and forth* movement of the domain walls because of the extremely large spontaneous strain for this crystal (§ 4). However, in the following sections we shall treat the present problem within the framework of ferroicity, rather than merely as a twin-formation problem, for the following reasons.

(i) The necessary condition that a ferroelastic crystal should have *at least* two identical or enantiomorphous orientation states is satisfied in the present case. It is clear from the work of Ramachandran & Lonappan (1957) that the crystal structures across the wall DW1 are indeed equivalent (enantiomorphous); this plane is a pseudo-glide plane of symmetry.

(ii) The fact that new domains of finite, non-zero thickness (of the order of a few micrometres) can be created *implies* that the domain walls separating these new, thin, domains from the neighbouring domains must be moving also (albeit in one direction, say forward, only, and over distances of the order of a few micrometres only).

(iii) Ascribing ferroelastic behaviour to KClO_3 enables one to provide a rather satisfying phenomenological basis for the observed systematics of domain structure in this crystal.

3. Choice of the prototype

For a proper characterization of a ferroelastic crystal, it is essential to determine its prototype symmetry also (Aizu, 1970a; Cracknell, 1974). For KClO_3 , if the orthorhombic phase above the reported transition temperature of 523 K were the prototype phase, only

two types of domain walls, namely $x = 0$ (bc planes) and $z = 0$ (ab planes, or c planes) should occur in the monoclinic phase (Sapriel, 1975). We have seen above, however, that at least four different types of domain walls occur in the monoclinic phase. Thus mmm is ruled out as the prototype symmetry.

DTA and DSC experiments do not reveal any further phase transitions before the crystals melt at 632 K (Deshpande, Mirza & Phadnis, 1979). The absence of these transitions was further confirmed by monitoring the birefringence of these crystals as a function of temperature by the rotating-analyser method (Wood & Glazer, 1980).

The prototype phase for KClO_3 is thus hypothetical. Assuming that all the phase transitions involved are either continuous or only weakly discontinuous (so that the Landau theory of phase transitions is applicable), one expects the prototype symmetry to be such that both $2/m$ and mmm symmetries are its subgroups. This leaves us with the following four possibilities: $m3m$, $m3$, $6/mmm$ and $4/mmm$.

The point group $m3$ can be rejected as a probable prototype symmetry, because it requires the occurrence of three mutually perpendicular domain walls (Sapriel, 1975), which is contrary to the observed domain structure. $6/mmm$ can also be rejected because it fails to account for the occurrence of domain walls DW3 and DW4.

Out of the three possible Aizu species with a $4/mmm$ prototype for the present case, only one can explain the observed domain structure. This is $4/mmm F 2/m(s)$, with the monoclinic axis of the ferroelastic phase at an angle of 45° to the x axis in the z plane. We accordingly assign KClO_3 to this species.

Before describing the consequences of this assignment, we may state here that the remaining possible prototype symmetry, namely $m3m$, is also compatible with the present choice. $m3m$ is a supergroup of $4/mmm$. Therefore the observed domain structure can also be explained by choosing $m3m F 2/m(s)$ as the correct Aizu species. On the other hand, if $m3m$ is indeed the true prototype symmetry, as many as 45 different types of domain walls should be observable in the monoclinic phase, assuming that KClO_3 in this phase is a *full* ferroelastic. The actual number observed is only four. Therefore, KClO_3 is either a *partial* ferroelastic with a cubic prototype (and a tetragonal intermediate phase), or a full ferroelastic with a tetragonal prototype.

The only indication we have so far for the possibility of partial ferroelasticity is that the crystal makes an antiferrodistortive phase transition (to an orthorhombic phase) and may therefore, presumably, be an *improper* ferroelastic [see, for example, Janovec *et al.* (1975) for a discussion of the relationship between partial ferroics and improper ferroics]. On the other hand, some evidence for proper (and therefore full) ferroelasticity

comes from the fact that the magnitude of spontaneous strain, calculated by choosing the tetragonal prototype (see § 4), varies linearly as the square root of temperature, implying a mean-field type of behaviour (Fig. 5). Such behaviour is to be expected for most of the proper ferroelastics (Cowley, 1976).

In the absence of any further evidence to the contrary, we shall work with a tetragonal prototype in what follows.

We postulate the following lattice vectors as corresponding to the true lattice vectors of the tetragonal prototype phase (Fig. 1b):

$$\mathbf{a}' = (\mathbf{a} - \mathbf{b})/2; \quad \mathbf{b}' = (\mathbf{a} + \mathbf{b})/2; \quad \mathbf{c}' = \mathbf{c} - \mathbf{a} = 2\mathbf{c}_0. \quad (2)$$

The corresponding distorted tetragonal cell has the following lattice parameters: $a' = b' = 3.633$, $c' = 14.170 \text{ \AA}$, $\alpha' = \beta' = 102.71^\circ$, $\gamma' = 100.48^\circ$.

The reasons for postulating the above orientation of the prototype unit cell are as follows:

(i) $\tan^{-1}(a/b) = 39.76^\circ$, which is very close to the angle 40° between the b axis and the traces of DW3 and DW4 (§ 2).

(ii) $\sin^{-1}(a/2c_0) = 19.14^\circ$, which is fairly close to the observed inclination, 21° , of DW2 (§ 2).

(iii) Crystal habit is sometimes indicative of the prototype symmetry. In the present case, the most frequent habit is that of rhombus-shaped plates or blocks with edges parallel to the vectors \mathbf{a}' , \mathbf{b}' , \mathbf{c}' defined above. (The rhombus angle of 100° in Fig. 3 is to be compared with the angle $\gamma' = 100.48^\circ$.)

For the Aizu species $4/mmm F 2/m(s)$, the deviatoric part of the spontaneous strain tensor can be written as follows (Aizu, 1970b):

$$\begin{bmatrix} 0 & A & C \\ A & 0 & C \\ C & C & 0 \end{bmatrix}$$

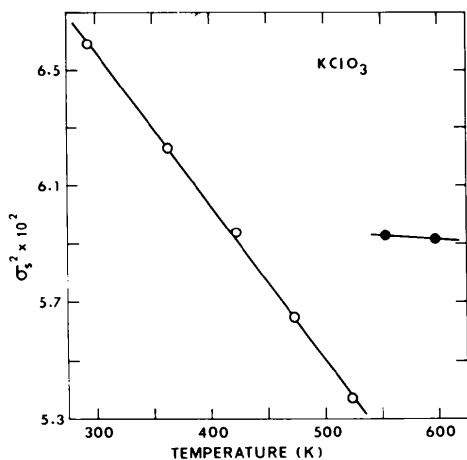


Fig. 5. Plot showing the variation with temperature of the square of the spontaneous strain, as calculated from the variation of the lattice parameters. There is a discontinuity in the curve at the monoclinic to orthorhombic phase transition.

For KClO_3 at room temperature (293 K),

$$A = (\pi/2 - \gamma')/2 = -0.0914, \quad (3)$$

$$C = (\pi/2 - \beta')/2 = -0.1109. \quad (4)$$

Nine types of domain walls are expected for a ferroelastic phase belonging to the above species. Their equations, with reference to a Cartesian frame fixed in the prototype phase, are as follows (Sapriel, 1975):

$$z = 0; \quad (5)$$

$$x = -y; \quad (6)$$

$$x = 0; \quad (7)$$

$$y = 0; \quad (8)$$

$$x = y; \quad (9)$$

$$Ay \pm Cz = 0; \quad (10)$$

$$Ax \pm Cz = 0. \quad (11)$$

The observed domain walls DW1, DW2, DW3 and DW4 can be taken to correspond to (5), (6), (7) and (8) respectively.

The present choice of the prototype and the above identification of domain walls also explains, at least qualitatively, the observed inclination of 21° of DW2 from the normal to the c face. This results from a spontaneous shear of the prototype lattice in the b plane, along the direction of \mathbf{a} (Fig. 1). The same postulated shear also explains the tilt of DW3 and DW4. If the magnitude of the shear is such that \mathbf{c}' is turned by 21° in the b plane, then the component of this tilt at an angle of 40° to the shear direction should be smaller by a factor of $\cos 40^\circ$ (neglecting any anisotropy of the shear elastic constants). That is, the tilt for DW3 and DW4 should be $\sim 16.2^\circ$. The measured value is 17° . [This fact is also reflected in Fig. 4, where the normals to DW2, DW3, and DW4 all lie on the same great circle (the dashed line).]

Domain walls corresponding to (9), (10) and (11) have not yet been observed.

4. Magnitude of spontaneous strain

The above model implies an extremely large value for the spontaneous strain at room temperature. The magnitude of spontaneous strain, σ_s , as defined by Aizu (1970b), is given by

$$\sigma_s^2 = 2A^2 + 4C^2,$$

so that $\sigma_s = 0.257$ at 293 K. This value of σ_s is the highest reported so far,* higher even than that for

* It may be mentioned here that the choice of a cubic prototype, rather than the tetragonal one (see § 3), will mean a still higher estimated value of σ_s at room temperature. This is because of the additional contribution to σ_s from the diagonal terms of the strain tensor for the cubic case.

H_3BO_3 crystals (Wadhawan, 1978a). Such a large σ_s indicates that the hypothetical prototype phase (for which $\sigma_s = 0$) can be realized in this case at a rather high temperature only. Fig. 5 shows the variation of σ_s^2 with temperature, calculated from the X-ray thermal-expansion data of Lonappan (1955) and Ramachandran & Lonappan (1957). The variation (in the monoclinic phase) is linear and extrapolates to $T = 1544$ K for $\sigma_s^2 = 0$.

If the spontaneous strain is indeed so large at room temperature, it can be expected to limit greatly the thickness of the new twin domains that can be created in an untwinned crystal. Let us take twinning across DW2 as an example. Since the angle between the c -face normal and the c' axis is 19.63° (Fig. 1a), the c faces of the twin components across DW2 will be inclined to each other by 39.26° . In a thick crystal, the creation of the second twin component from the first, and its growth (under the action of external uniaxial stress), will therefore create a large amount of strain. The crystal can relieve this strain by forming another twin wall, DW2, parallel to the first one and at a short distance from it, such that across the second wall the shear is in the opposite direction to that across the first. It then follows that, for a given crystal thickness, the thickness of the new, sandwiched, twin component will be small if σ_s is large. It can be taken as evidence of large σ_s in KClO_3 that no new twin components greater than a few micrometers thick could ever be created artificially.

In contrast to this, in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals for example, for which σ_s is not large (it is only 0.014), new twin domains of any thickness can be easily created even in thick crystals (Wadhawan, 1978b).

5. The orthorhombic phase

If one continuously watches through a polarizing microscope the changes occurring in an untwinned c_0 -axis needle of KClO_3 as its temperature is gradually increased through the monoclinic to orthorhombic phase transition, the following events are seen. When the crystal approaches the transition temperature, suddenly a few narrow twin components bounded by domain walls DW1 appear at some isolated sites along the length of the needle. (The crystals have a tendency to fly away in this temperature region.) More and more twin walls are then formed in rapid succession until they fill the whole crystal. After this, the domain walls gradually begin to disappear. Finally, when the transition to the orthorhombic phase is complete (at 560 K), the crystal is once again free from all DW1 twin walls. On cooling back through the transition, many of these walls reappear (at 552 K), with a thermal hysteresis of 8 to 10 K. The mean transition temperature, 556 K, determined here, differs con-

siderably from the value 523 K reported in the literature (Ramachandran & Lonappan, 1957; Pistorius, 1970).

The above discrepancy was confirmed by our birefringence measurements, normal to c plates, as a function of temperature. These gave the mean transition temperature at 553 K, and the same thermal hysteresis as above.

An examination of the crystal structure of this phase, as determined by Ramachandran & Lonappan (1957), suggests the possibility of antiferroelasticity in this phase. A necessary (though not sufficient) condition for this is that the ferroelastic to antiferroelastic phase transition be of first order (Aizu, 1969). This is indeed so in the present case.

Crystals containing domain walls DW2, DW3 or DW4 are found to retain them in the orthorhombic phase. DW3 and DW4, of course, are *not* expected to disappear according to our model. The reason for the apparent survival of DW2 is not yet clear. It is possible that these walls only *appear* to be retained, probably because of the damage caused by the large spontaneous strain to the surrounding lattice when these walls are created.

6. Discussion

According to Wyckoff (1964), the KClO_3 structure can be regarded as a distortion of the NaCl arrangement. Although we have chosen a tetragonal prototype for KClO_3 , it was pointed out in § 3 that a cubic prototype with the same orientation of the unit cell as that of the chosen tetragonal cell (and with cell lengths a' and b' quadrupled) can explain the observed domain structure equally well. As is to be expected, our domain-structure considerations lead us to postulate the same orientation of the distorted tetragonal (or cubic) prototype unit cell as is arrived at by an analysis of the atomic coordinates.

The magnitude of spontaneous strain, σ_s , for KClO_3 turns out to be 0.257 at room temperature. Such gigantic spontaneous strains were probably not visualized by Aizu (1970a) when he introduced the concept of ferroelasticity. However, we do not see any reason why we should insist on only 'small' lattice strains (of the order of 10^{-2} or less) when defining a ferroelastic. A large σ_s at any given temperature simply means that the transition temperature, above which the prototype phase is realizable, is very far away.

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The Use of Anomalous Scattering Effects to Phase Diffraction Patterns from Macromolecules

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Abstract

Recent experiments using synchrotron radiation to measure anomalous scattering terms at wavelengths very close to *L*-shell elemental absorption edges [Phillips, Templeton, Templeton, & Hodgson (1978). *Science*, **201**, 257–259] have demonstrated that effects much larger than those expected on the basis of simple atomic scattering calculations are observed. These observations of the large wavelength dependence of the magnitudes of anomalous scattering terms has prompted our reexamination of how such effects can be used to phase single-crystal diffraction patterns. This paper describes a methodology for using information on the magnitude of anomalous scattering effects to plan a multiple-wavelength phasing experiment on a macromolecule-containing crystal. Different data collection strategies, such as measuring data at many wavelengths less accurately or at a few wavelengths

accurately, are compared. The method uses principles taken from standard MIR phasing techniques and also can be used to process multiple-wavelength data to obtain the phases. A numerical example of phasing, using the anomalous scattering curves determined experimentally for cesium, is presented and the results discussed in terms of the applicability of multiple-wavelength phasing for protein crystallographic studies. A survey of a variety of heavy metals suggests that large changes in anomalous scattering near the *L* absorption edges are quite general and will be of importance in multiple-wavelength phasing of single-crystal protein diffraction patterns.

Introduction

It has long been apparent that anomalous scattering can be used to solve the 'phase problem' in crystallography. The experiment is best performed using a synchrotron radiation source, as the largest anomalous scattering effects are obtained only when the wave-

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