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NEUTRON SCATTERING STUDIES OF SOLID ELECTROLYTES *

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INTRODUCTION

Neutron scattering is now a well-established technique for probing atomic positions and motions in a solid or liquid.¹ To a first approximation the neutron impinging on a sample is scattered by the nuclei and the energy and momentum of the scattered neutron is determined by the collective nature of the sample's nuclei (coherent scattering process) or by the individual atom's motion (incoherent scattering process).

The conservation laws of momentum and energy in a scattering process are

$$\begin{aligned}\vec{Q} &= \vec{k}_i - \vec{k}_f \\ \hbar\omega &= \frac{\hbar^2}{2m_N} (k_i^2 - k_f^2)\end{aligned}\quad (1)$$

$\vec{Q}$ and $\hbar\omega$ are the crystal momentum and energy, k_i and k_f are the initial and final momentum of the neutron, and m_N is the mass of the neutron. Neutron scattering offers important advantages over optical and x-ray techniques. Because k_i is comparable to Q_{ZB} , the size of the Brillouin zone ($\sim 5\text{\AA}^{-1}$), studies of excitations throughout the Brillouin zone are possible. In light scattering $k_i \ll Q_{ZB}$ and

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only excitations very near the zone center are studied. Since the neutron energy is also comparable to the lattice vibrational frequencies (1-50 meV) studies of the lattice modes can be performed. In x-ray scattering the x-ray energy is much greater than the lattice frequencies and energy analysis with sufficiently high resolution is presently impossible. The scattering amplitude for neutrons has a limited variation over the periodic table whereas the scattering amplitude for x-rays is proportional to Z^2 , the charge in the nucleus. Thus neutrons allow visibility of light elements when heavier atoms are present.

In this talk I shall review some of the general formalism for elastic and inelastic neutron scattering and demonstrate what quantities can be measured. Next I shall show how neutron scattering has been applied to the studies of three different problems: 1) the anion disorder in the fluorite systems; 2) the dynamical behavior in the beta-alumina; and 3) the cation diffusion in αAgI .

The scattering cross section for neutrons is the sum of a coherent and an incoherent part. Dealing first with the coherent scattering, the partial differential cross section for a solid is:^{1,2}

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} |F(\vec{Q}, \omega)|^2 \quad (2)$$

where $F(\vec{Q}, \omega)$ is the generalized structure factor. It is composed of an elastic part which measures the average structure and an inelastic part which probes the time dependent fluctuations in the average structure. In the harmonic approximation

$$|F(\vec{Q}, \omega)|^2 = (2\pi)^3 \frac{N}{V} |F_0(\vec{Q})|^2 \delta(\vec{Q}-\vec{G}) \delta(\hbar\omega) + \sum_s |g_s(\vec{Q})|^2 (n(\omega)+1) \delta(\vec{Q}\pm\vec{q}-\vec{G}) \delta(\hbar\omega\pm\hbar\omega_s) \quad (3)$$

Here N is the number of unit cells in a crystal, V is the volume of the unit cell, $\vec{G}$ is a reciprocal lattice vector and $\vec{q}$ is the wave vector reduced to the first Brillouin zone. s denotes the mode of wave vector $\vec{q}$ and branch j . $n(\omega)+1 = \{ (\exp(\hbar\omega/kT))^{-1} + 1 \}^{-1}$ is the population factor

for creation of a phonon. The first term in Eq. (2) is the structure factor for elastic Bragg scattering

$$F_0(\vec{Q}) = \sum_k b_k e^{i\vec{Q} \cdot \vec{R}_k} e^{-W_k(\vec{Q})} \quad (4)$$

where R_k is the position of the k th atom in the unit cell and $W_k(\vec{Q})$ represents the Debye-Waller factor. This is valid for point particles whose position is smeared out by their thermal motions. Eq. (4) can be written in a more general way by introducing an average density:

$$\rho(\vec{r}) = \sum_k b_k e^{-W_k(\vec{Q})} \delta(\vec{r} - \vec{R}_k)$$

and $F_0(\vec{Q})$ becomes

$$F_0(\vec{Q}) = \int_{\text{cell}} \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r} \quad (4')$$

For solids with long range order elastic peaks appear at well-defined positions in reciprocal space which satisfy the δ function, namely $\vec{Q} = \vec{G}$. If the long range order is interrupted due to some defects, the Bragg scattering now represents the scattering from an average cell. By examining the intensities of these peaks one can obtain an effective value of the scattering strength $b'_k = m_k b_k$ where m_k is the fractional occupancy of the k th atom at site R_k . In a disordered system additional scattering appears which is not as well localized in reciprocal space. Its intensity and q width is related to the size of the disordered regions and the interaction among the defects. It is measurements of this diffuse scattering that provides detailed information of the disorder occurring in many solid electrolytes and has been amply discussed for the x-ray case by R. Comès.³

The second term in Eq. (2) is the dynamical structure factor for coherent inelastic scattering:

$$S_s(\vec{Q}) = \sum_k \frac{b_k(\vec{Q} \cdot \vec{\xi}_{s,k})}{(2NM_k \omega_{s/k})^{1/2}} e^{i\vec{Q} \cdot \vec{R}_k} e^{-W(\vec{Q})} \quad (5)$$

By satisfying the 6 functions in Eq. (2) with a judicious choice of incident and scattered neutron momentum the phonon dispersion curves can be measured. Additionally, the eigenvector of the atomic displacements, ξ_k , determines the intensities of the scattered neutrons. If there is disorder in the solid or there are important anharmonic effects the normal modes become less well defined and the observed spectra contain a measurable energy width. Below I shall show how inelastic neutron scattering has provided some key information into the lattice dynamical behavior of the beta alumina electrolytes.

The coherent scattering cross section discussed above probes the correlations of pairs of particles distributed in space. The incoherent scattering, on the other hand, probes correlations of individual particles with themselves. The time dependence of these correlations is related to the motion of the isolated atoms which can usually be described by a diffusion process. If the atom diffuses freely over the entire sample the neutrons scattered by it will have a slightly different energy. The resulting spectra will show a quasielastic peak whose width is proportional to the diffusion constant of the material. Neutron scattering offers the possibility of simultaneously measuring the time scale of the diffusion via the energy width and the spatial correlations via the Q dependence of the scattering. Hydrogen has an exceptionally large incoherent scattering strength and the studies of the quasielastic scattering from the hydrogen atoms has provided valuable data about the diffusive processes of hydrogen dissolved in metals.⁴ Similar techniques have been applied to the superionic conductors. Axe et al.⁵ have measured the rotational diffusion of NH_4^+ in beta alumina and Eckold et al.⁶ have used the incoherent scattering from silver ions to study the diffusion processes in $\alpha\text{-AgI}$.

TECHNIQUES

There are two conventional types of inelastic neutron scattering spectrometers: a Triple-Axis Spectrometer (TAS) or a Time-of-Flight Spectrometer (TOFS). I shall not go into the details of these instruments since they are well described in the literature^{1,2,7}, but I would like to discuss where each spectrometer is most applicable. The

energy and momentum transfer ranges covered by these instruments with existing apparatus are: $0.005 < \hbar\omega(\text{meV}) < 300$ and $0.02 < Q(\text{\AA}^{-1}) < 20$. The TAS is most useful for single crystal spectroscopy where one has flexibility to scan along a chosen direction in $\hbar\omega$ - q space. The conventional types of scans are either constant Q scans (where the energy is varied) or constant E scans (where the momentum is varied). These methods are most useful in measuring phonon dispersion curves in solids.

In polycrystalline materials where the momentum direction does not play an important role, or in systems where the scattering is nearly isotropic as for incoherent scattering, the TOFS is a more efficient instrument. In these instruments the scattering angle is kept constant and the scan is along an oblique direction in ω - q space as energy is transferred to the sample. The added efficiency of this instrument is the ability to measure several scattering angles simultaneously by use of multiple detectors. Since the time for the neutron to travel a known path is being measured the entire energy spectrum at each angle is obtained for a given counting period. Below I shall discuss the results of Eckold et al.⁶ who have measured the diffusion processes in a polycrystalline sample of α -AgI using a TOFS.

A most interesting property to measure in the super-ionic conductors is the diffusion constant, D , of the conducting species. To set the scale of what energy resolution is needed consider a diffusion constant $D = 10^{-5} \text{ cm}^2/\text{sec}$. The observed quasielastic line width (Γ) at a $Q=0.5 \text{ \AA}^{-1}$ (assuming simple diffusion) is $\Gamma=2DQ^2=0.2 \text{ meV}$ a value obtainable with conventional instruments. However, for solid electrolytes neutron scattering methods have been utilized only in α -AgI⁶ and NH_4 -beta alumina⁵ to measure the diffusive motion. Na^+ and Ag^+ -beta alumina possess diffusion constants of $\sim 10^{-5} \text{ cm}^2/\text{sec}$ near $T=400^\circ\text{C}$ and should be measurable.⁸

DEFECT STRUCTURE IN FLUORITES

Fig. 1 shows the face centered cubic structure of the fluorite class of ionic conductors. The cation (Ba or Pb

in our study) is located at the cube center of Fig. 1 and surrounded by 8 fluorines which occupy tetrahedral interstices (FI sites) of the cation sublattice. As the material is heated it is the anion that disorders and contributes to the high ionic conductivity.⁹ Some of the fluorine ions move from their regular (FI) positions and occupy the empty octahedral positions (FII) denoted by "x" in Fig. 1. The redistribution of the fluorine ions with rising temperature causes an anomaly in the heat capacity at temperatures near the melting temperature.¹⁰ For BaF_2 ¹¹ and PbF_2 ¹² the heat capacity and ionic conductivity indicate that there is a smooth or "diffuse" phase transition which can be associated with fluorine disordering.

Elastic neutron scattering experiments were performed on polycrystalline samples of BaF_2 and PbF_2 in order to measure directly the anion disorder. The details of the experiment will be published elsewhere¹³ but we essentially performed accurate intensity measurements of as many reflections as possible (about 20 at room temperature and ~ 15 near the melting point). These intensities are proportional to $|F_o(Q)|^2$ of Eq. (4). One common way of obtaining the disordered structure would be to assume a model of the disorder and perform a least-squares fit to the observed intensities allowing the R_k 's and $W_k(Q)$'s, and the occupancies to be adjustable parameters. An alternative method that we adopted is to calculate directly the nuclear density in real space by taking the Fourier inversion of the observed structure factors. The average nuclear density in the unit cell obtained from Eq. (4') is:

$$\langle \rho(\vec{r}) \rangle = \frac{1}{V_c} \sum_{\vec{G}=-\infty}^{\infty} F_o(\vec{G}) e^{-i\vec{G} \cdot \vec{r}} \quad (6)$$

This Fourier method is usually quite difficult in complicated structures because it requires the knowledge of the phase of the structure factor for each reflection. However, for the simple fcc fluorite lattice the phase can be obtained by calculating from the known atomic arrangement of the ordered structure. An additional problem arises due to the limited number of reflections measured such that the sum in Eq. (6) is not complete. This results in termination errors which can yield nonsensical negative scattering densities. This is solved by multiplying the structure

Fig. 1. Fluorite structure

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by an apodizing function (well known in optical interferometry¹⁴) which gives strong weight to the small G reflections and forces the large G reflections to be negligible. The Fourier inversion of the apodized structure factor smears out the nuclear density over a region determined by the size of the apodizing function. This sets a limit to the resolution of the Fourier method. We used as an apodizing function a cube in real space. The size of the cube was chosen such that the densities of the ordered fluorite structure were reproduced at room temperature.

Fig. 2 shows a portion of our BaF_2 results for the nuclear densities in the region of the fluorite cell encompassed by the dashed lines of Fig. 1. This is a difference plot in the nuclear density between 1100°C and 25°C : $\rho(1100^\circ\text{C}) - \rho(25^\circ\text{C})$. The top of the figure shows the resolution of this method where δ represents the size of the apodizing box. It can be seen that the barium density has spread out compared to room temperature. This is expected because of the large thermal motions generated by the high temperature, which appears as an increased Debye-Waller factor in Eq. (4). A similar effect appears for the normal fluorine sites, FI. The new feature is the appearance of additional fluorine density centered at FII. There is no

Fig. 2. Difference in the nuclear densities between 1100°C and 25°C for BaF₂.

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evidence that the fluorine atoms occupy off-centered positions as obtained from substitutionally induced disorder in other fluorite systems.¹⁵

In order to obtain quantitative information we can calculate the total nuclear density near the Ba, FI, and FII sites. This is obtained by dividing the fcc cell into Wigner-Seitz cells centered at the Ba, FI, and FII positions. In this way all the space is filled. The integrated densities for the k th atomic species, $n(k)$, normalized to the ordered densities is shown in Fig. 3a for BaF₂ and Fig. 3b for PbF₂. For both systems the metal densities remain constant over the entire temperature range as expected. The FII densities initially are zero at room temperature but begin to increase as the temperature is raised. They reach a value of ~40% for BaF₂ and PbF₂ just below the melting points. ($n(\text{FI})$ is not shown but can be obtained from the obvious fact the $n(\text{FI}) + n(\text{FII}) = 1$.)

We now have a quantitative measure of the amount of disorder. An order parameter for this phase transition can be defined:

Fig. 3. (a) $n(\text{Ba})$, $n(\text{FII})$ and η for BaF_2 . The curve is the result of simple alloy theory described in the text. (b) $n(\text{Pb})$, $n(\text{FII})$ and η for PbF_2 . The curve is a guide to the eye.

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$$\eta = 3n(\text{FI}) - 2$$

$$\text{or } \eta = 1 - 3/2 n(\text{FII})$$

The order parameter satisfies the conditions that $\eta=1$ in the ordered state ($n(\text{FII})=0$ and $n(\text{FI})=1$) and $\eta=0$ in the disordered state ($n(\text{FI})=n(\text{FII})=2/3$). The transition can be analyzed in the mean field or Bragg-Williams approximation by using conventional alloy theory.¹⁶ The configurational energy E can be calculated and one obtains:

$$E = \beta\eta + \gamma\eta^2 \quad (7)$$

where β is proportional to the single particle energy and γ represents the interaction between the FI and FII fluorines. Once the configurational entropy, W , is calculated the free energy becomes

$$F = E - kT \ln W \quad (8)$$

By minimizing this expression with respect to η the

temperature dependence of the order parameter is obtained by solving the following expression:

$$\frac{2(1-\eta)^2}{(\eta+2)(2\eta+1)} = \exp\left(\frac{9}{2kT}(\beta+2\gamma\eta)\right) \quad (9)$$

The temperature dependence for η with $\beta=0$ is shown in Fig. 3a as the solid line. It agrees reasonably well with our experimental data for BaF_2 . This solution $\gamma \neq 0$ suggests that strong collective effects between the fluorines play an important role in the disordering and thus the conductivity. For PbF_2 the situation is not as clear and no simple approximation of Eq. (9) reflects the behavior of the order parameter.

For BaF_2 the order parameter shows a featureless smooth change as the melting temperature approaches. This is true of the conductivity also; there is no evidence of an anomalous change as the sample is heated to the melting point.³ For PbF_2 , however, there is a rapid change in the order parameter centered about $T \sim 750^\circ \text{K}$. This corresponds closely with the behavior of the ionic conductivity¹² which also shows a rapid variation in the same temperature region.

BETA ALUMINA

The most widely studied solid electrolytes are the beta aluminas.⁸ We have measured the dispersion of the low frequency lattice modes in an effort at understanding the lattice dynamics of these materials.¹⁷

Recent optical measurements have revealed lattice vibrations whose frequencies are very sensitive to the type of cation.^{18,19} These modes were interpreted as the attempt frequency for the diffusing ion in a random-hopping model of diffusion. They were treated as Einstein-like oscillators since the cation is moving independently of the host lattice. Fig. 4 shows the dispersion of the low frequency modes along the two high symmetry directions in the mirror plane for Na-beta alumina. The normal longitudinal and acoustic modes are observed in addition to several optical branches. A striking feature is a branch at $\sim 6 \text{ meV}$ which shows very little dispersion. It is this mode that is

Fig. 4. Phonon dispersion curve for Na-beta alumina. Neg. #5-19-76

assigned to the cation vibration. The weak dispersion is evidence that the mode is truly Einstein-like and moves independently of the rest of the lattice. This mode is only seen when the mirror plane coincides with the scattering plane, which proves that the displacements are confined to the mirror plane. Fig. 5 shows the spectra of this mode at two different Q values. The intensity is weak compared to the other modes in this crystal. This is expected for the cation vibrations since only 4% of the atoms are contributing to the scattering. The energy width is ~ 2.5 meV which is much larger than the instrumental resolution (0.8 meV). This suggests that there is a finite lifetime of this mode of $\sim 3 \times 10^{11}$ sec $^{-1}$. Another possibility to explain the broadening is that there are more than one excitation in this frequency region and our resolution is insufficient to resolve them. Recent infrared transmission studies do observe several overlapping modes in this frequency region.²⁰

Substitution of Ag^+ for Na^+ in the beta alumina host changes the low frequency spectra drastically as shown in Fig. 6 and observed in the optical measurements.^{18,19} Instead of a well-defined propagating excitation there now is a broad feature centered about $\hbar\omega=0$ meV. As the temperature

Fig. 5. The cation mode in Na-beta alumina. Neg. #5-18-76

is decreased the line width remains constant but the intensity drops due to the temperature factor in the dynamical structure factor, Eq. (5). There also is no change in the line width as the sample is heated to 425°C. It is not understood why no well-defined excitations are observed since the optical measurements show features in the 3-4 meV range.^{18,19} It is likely that there is enough dispersion in these low frequency optical branches that the neutron scattering sees some average of several overlapping, damped excitations.

The energy line width of the E=0 component in Fig. 6 is resolution limited. We attempted to measure the line width at temperatures up to T=425°C in an effort to observe any diffusion broadening. Even with a resolution of 0.24 meV no broadening was observed.

The intensity of the central E=0 component of Fig. 6 shows a strong temperature dependence. This is shown more clearly in Fig. 7 where E=0 scans are performed along the $[\xi\xi\cdot 0]$ direction. At room temperature there is a broad asymmetric peak centered about $\xi \sim 1.65$ which is most likely related to the general disorder in the solid. As the temperature is cooled a sharp peak develops at $\xi \sim 1.35$ which

Fig. 6. Inelastic spectra of Ag-beta alumina. Neg. #5-13-76

becomes very intense at 26 K. This is similar to the x-ray results of LeCars et al.²¹ who interpreted this scattering as an ordering of the Ag^+ sublattice. There are, however, some important differences between the neutron and the x-ray results. At room temperature the x-ray studies observe a spot at $\xi=4/3$. Since the x-ray technique automatically integrates over energy it cannot distinguish between dynamical or static phenomena. In Fig. 7 the spectrometer is set for zero energy transfer and only dynamical behavior with frequencies within the instrumental resolution (0.8 meV) is observed. Since at room temperature no spot-like scattering is observed we conclude that the feature in the x-ray experiment must be due to some dynamical cation motion with relatively large frequency.

QUASIELASTIC SCATTERING IN α -AgI

Quasielastic neutron scattering experiments were performed by Eckold et al.²² on α -AgI at $T=250^\circ \text{C}$ where they successfully measured the diffusion motion of the Ag^+ ion. The experiments were performed with the multichopper TOFS, IN5 at the Institut Laue-Langevin. Their results are shown in Fig. 8 for two different scattering angles. The

Fig. 7. $E=0$ scan along $[\xi\xi\cdot 0]$ for several temperatures.

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observed scattering was assumed to come from only the Ag ions. These spectra are composed of two distinct features: a narrow peak centered about $\Delta\omega=0$ which has an energy width larger than the instrumental width; this is resting on top of a much broader peak which has a larger width and a strongly Q dependent intensity. No simple model of translational diffusion can explain these spectral shapes. Eckold et al assumed that there were two types of motion of the Ag^+ ion on two different time scales. The broad peak arises due to a diffusive "local" motion within a restricted region of space given by the structure of the iodide ion lattice. The narrow peak is due to a translational diffusion over the entire crystal volume. This latter component corresponds, at small Q , to the diffusion measured by the tracer method.

The model proposed for the translational jump diffusion process consists of a mean residence time τ_0 , a jump time τ_1 , and a jump length l . In most discussions of jump diffusion the jump time is instantaneous: $\tau_1 \rightarrow 0$. However, in this case a non-zero value of the jump time is necessary in order to fit the data. For the local motion it was assumed that the Ag^+ ion diffuses within a limited spherical region of radius r . It was further assumed that the Ag^+

Fig. 8. Experimental quasielastic neutron scattering spectra of α -AgI at two different scattering angles. The solid lines result from a model calculation. Neg. #5-17-76

ions move along the surface of the sphere with a rotational diffusion constant D_r . The results of the fit of their model with the data is shown in Fig. 8 and the agreement is quite good. The values of the parameters obtained from this model are also given for the two angles measured. It is seen that the jump time is roughly one-half of the residence time.

It now appears that the diffusion of Ag^+ ions in AgI is composed of a large amplitude local random motion superposed with a translational jump diffusion with a finite jump time.

CONCLUSION

I have demonstrated how neutron scattering can play an important role in determining the nature of the disorder and the conducting mechanism in the solid electrolytes. There remains much to understand, especially in the studies of the β -alumina systems. It is expected that as new electro-

lytes are developed neutron scattering techniques will continue to play a fundamental role in understanding their behavior.

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REFERENCES

1. See Thermal Neutron Scattering, Ed. P. A. Egelstaff (Academic Press, New York, 1965).
2. B. N. Brockhouse, in Phonons and Phonon Interactions, Ed. T. A. Bak (W. A. Benjamin, Inc. New York, 1964) p. 221.
3. R. Comès, these Proceedings.
4. T. Springer in Springer Tracts in Modern Physics, (Springer, Berlin, 1972) Vol. 64.
5. J. D. Axe, L. M. Corliss, J. M. Hastings, and W. L. Roth, these Proceedings and to be published.
6. G. Eckold, K. Funke, R. E. Lechner, and J. Kalus, Phys. Letters 55A, 125 (1975); J. Phys. Chem. Solids, to be published.
7. R. Pynn in Methods in Computational Physics: Advances in Research and Applications, Vol. 15 (Academic Press, New York, 1976).
8. J. T. Kummer, Progr. Solid State Chem. 7, 141 (1972).
9. M. O'Keefe in Fast Ion Transport in Solids, W. Van Gool (North-Holland, Amsterdam, 1973).

10. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 72, 1277 (1968).
11. V. R. Beloslouov, R. I. Efremova, and E. V. Natizen, Soviet Phys. Solid State 16, 847 (1974).
12. C. E. Derrington, A. Navrotsky, and M. O'Keefe, Solid State Commun. 18, 47 (1976).
13. J. D. Axe, S. M. Shapiro, and N. Wakabayashi (to be published).
14. See J. Strong, Concepts of Classical Optics (W. H. Freeman & Co., San Francisco, 1958) p. 206.
15. A. K. Cheetam, B. E. F. Fender, and M. J. Cooper, J. Phys. C: Solid State Phys. 4, 3107 (1971); D. Steele, P. E. Childs, and B. E. F. Fender, J. Phys. C: Solid State Phys. 5, 2677 (1972).
16. M. A. Krivoglaz and A. A. Smirnov, The Theory of Order-Disorder in Alloys (MacDonald, London, 1964).
17. D. B. McWhan, S. M. Shapiro, J. P. Remeika, and G. Shirane, J. Phys. C: Solid State Phys. 8, L487(1975).
18. S. J. Allen, Jr. and J. P. Remeika, Phys. Rev. Lett. 33, 1478 (1974).
19. L. L. Chase, C. H. Hao, and G. D. Mahan, Solid State Commun. 18, 401 (1976); C. H. Hao, L. L. Chase, and G. D. Mahan, to be published in Phys. Rev. B.
20. S. J. Allen, Jr., F. DeRosa, and J. P. Remeika, Bull. Amer. Phys. Soc. 21, 284 (1976); and these Proceedings.
21. Y. Lefkars, R. Comès, L. Deschamps and J. Thery, Acta Cryst. A30, 305 (1974).