

High-pressure NMR investigations of the protonic conductor $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 1.5\text{H}_2\text{O}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 1495

(<http://iopscience.iop.org/0953-8984/1/8/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.90

The article was downloaded on 10/05/2010 at 17:50

Please note that [terms and conditions apply](#).

High-pressure NMR investigations of the protonic conductor $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 1.5\text{H}_2\text{O}$

D R Balasubramanyan† and S V Bhat

Department of Physics, Indian Institute of Science, Bangalore 560 012, India

Received 28 June 1988, in final form 22 September 1988

Abstract. The effect of high hydrostatic pressure up to 1.5 GPa on ionic motion in $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 1.5\text{H}_2\text{O}$ has been studied by wide-line ^1H NMR experiments performed in the temperature range from room temperature to 77 K. The experiments at room temperature have shown a large increase in the second moment at 0.45 GPa as a result of a pressure-induced phase transition. The temperature dependence study up to 0.425 GPa has shown a gradual increase in the values of activation energy and attempt frequency with increase in pressure. The activation volume for motion at 300 K has been estimated to be 6% of molar volume. Vacancy-assisted ionic jumps are concluded to be the mode of charge transport. Second moments estimated at 77 K show evidence for tunnelling reorientation of at least one of the two NH_4^+ groups in the compound.

1. Introduction

An early wide-line NMR study of ammonium ferrocyanide hydrate (AFC) (Whittingham *et al* 1972) showed that this material is a possible fast ion conductor even at room temperature. The authors observed narrowing of the ^1H resonance line in the temperature range 150–315 K. The linewidth was shown to decrease to values less than 0.01 mT due to the translational diffusion of the ions through the lattice which averages out the intermolecular dipolar interaction. The diffusion coefficient at 300 K was estimated to be $1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ with an activation energy of 19 kJ mol $^{-1}$. However, it was not possible from this study to determine the nature of the diffusing species, i.e. whether it is ammonium ions or protons themselves. The contribution of the protons of the water molecules to the signal could also not be determined and it was assumed that the water protons give rise to a broad undetectable base line drift under the much narrower ammonium signal. However, x-ray structural study of single crystals of AFC (Morosin 1978) has shown that there are two kinds of ammonium ions situated at two different crystallographic sites (b and g of space group $Ia3d$) with different bonding environments. The structural arrangement shows evidence for spiral paths connecting the 'b' NH_4 sites and the water molecules. The study proposed that ionic diffusion in this compound involves molecular groups rather than H^+ ions. Our own recent high resolution NMR study of AFC (Balasubramanyan and Bhat 1987) carried out at 270 MHz and 500 MHz has shown the presence of two chemically shifted signals attributed to NH_4^+ and H_2O protons. From the temperature dependence of linewidths and chemical shifts it was concluded that the protons of both NH_4^+ and H_2O take part in diffusion. With a view to

† Present address: Department of Physics, Regional Engineering College, Calicut 673 601, India.

throwing more light on the nature of ionic diffusion in this compound, we have carried out wide-line NMR studies of AFC from room temperature down to 77 K at high hydrostatic pressures. The room-temperature proton NMR spectra recorded at different pressures up to 1.5 GPa showed evidence for a phase transition in the compound at 0.45 GPa and this was confirmed by a compressibility study of the sample (Balasubramanian *et al* 1988). In this paper we present further results of these high-pressure studies. High-pressure NMR has been used in the past for the study of molecular motions in ionic solids. In addition to providing information on activation energies, activation enthalpies and phase transitions if any, such high-pressure studies give direct information on activation volumes which lead to a better understanding of the mechanism of ionic diffusion.

2. Experiment

Polycrystalline AFC purchased from the manufacturers, Aldrich Chemicals, was used without further purification. The sample was studied by thermogravimetric analysis (TGA) at a heating rate of 3 K per minute. The analysis showed that the sample loses the water of hydration in the temperature range 323–373 K. As the loss in weight is about 9% around 373 K the compound is most likely $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 1.5\text{H}_2\text{O}$. Since the material is hygroscopic it was dried by freeze–pump–thaw technique before transferring it to the Teflon sample cells. A home-built low-level Robinson oscillator working at 14 MHz was used for recording NMR spectra. Precautions were taken to avoid saturation and excess modulation broadening. Wherever it became necessary to use higher modulation suitable corrections were applied in the calculation of second moments using the formula of Andrew (1953). Spectra at high pressures were recorded using a home-fabricated (Ramanathan and Srinivasan 1978) lock-type Be–Cu pressure vessel designed to work up to 1.5 GPa. A Teflon cylinder of length 30 mm, outer diameter 15.8 mm and wall thickness 1 mm was used as the sample container. The entire sample cell was filled with the sample. Since Teflon is highly compressible and is also used as pressure transmitting medium, the pressure on the sample could be expected to be more or less hydrostatic. The error in the pressure measurements was estimated to be less than 15%. A controlled flow of cold nitrogen gas was used to vary the sample temperature. The accuracy in the measurement of temperature was ± 2 K. For experiments at 77 K the entire pressure cell containing the sample was immersed in liquid nitrogen.

3. Results and discussion

3.1. Second moment studies

The second moments of the room-temperature signals recorded at different pressures have been calculated and a plot of these values as a function of sample pressure is shown in figure 1. As seen from the plot the second moments are very small up to 0.4 GPa. A sudden and sharp discontinuity is observed at 0.45 GPa showing an increase by two orders of magnitude in the second moment. After that there is a plateau region from 0.45 GPa to 1.0 GPa in which the second moment remains practically constant at $(20.8 \pm 1.2) \times 10^{-3} \text{ mT}^2$. Thereafter there is again a gradual but small increase in the second moment up to 1.5 GPa. The occurrence of the plateau may be explained as follows. Whereas the hindering of the translational motion of the 'g' NH_4 groups is sudden resulting in the broad signal, the hindering of the motion of the 'b' NH_4 and H_2O

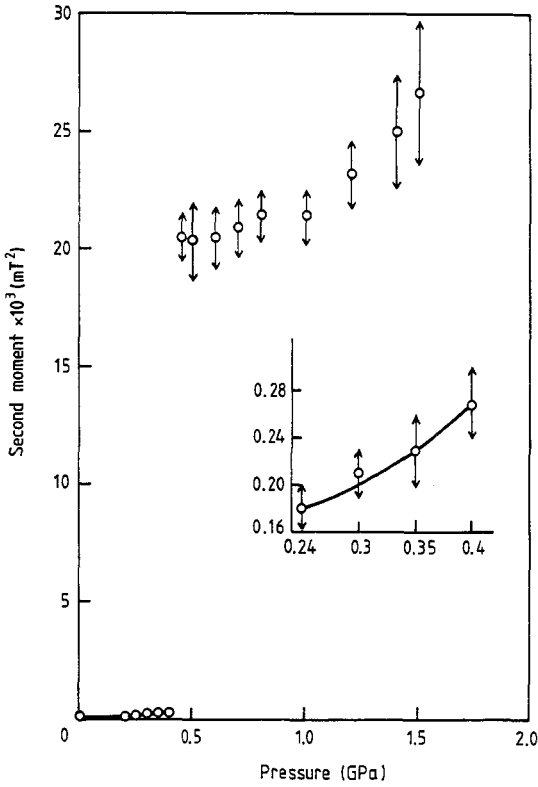


Figure 1. Variation of second moment with pressure at room temperature.

groups seems to be gradual as the narrow signal due to them can be seen even up to 1.2 GPa. However, the latter signal being weaker in intensity compared to the broad signal its contribution to the overall second moment is not appreciable resulting in the plateau region. The slight increase in the second moment in the pressure range 1.2–1.5 GPa and the disappearance of the narrow signal around 1.4–1.5 GPa shows the complete freezing of translational motion of all the mobile species in the compound.

3.2. Activation volume

In the study of ionic diffusion and other activated processes it is useful to define and determine an activation volume associated with the motion of the mobile species. In the absolute reaction rate theory this quantity which represents the contribution of the mobile species to the volume of the crystal is defined via the familiar expression for the Gibbs free energy (Samara 1984):

$$dG = VdP - SdT \tag{1}$$

from which we have

$$\Delta V_M = (\partial \Delta G / \partial P)_T \tag{2}$$

where ΔV_M is the activation volume for the motion and ΔG is the change in Gibbs free energy associated with the diffusive jump.

In the reaction rate theory, the motional activation volume ΔV_M represents the lattice dilation associated with the diffusive motion (jump) of the mobile species. A hard-sphere model suggests that ΔV_M should be approximately equal to the volume of

the diffusing species for vacancy and interstitial motion. But ΔV_M is generally found to be much smaller than that. The relatively small ΔV_M values reflect partially the fact that the real ions are not hard spheres and there is considerable relaxation around the defects (Samara 1984).

In the case of fast ion conductors the mechanism of ionic transport is different from that in normal ionic conductors. These materials are characterised either by the availability of a very large number of normally vacant lattice sites or by an essentially complete disorder of the mobile ionic species. This results in low activation energy and activation volume for such materials, reflecting the ease with which ionic transport takes place in these materials.

Although conductivity measurements at high pressures have been generally used for the determination of activation volumes in the case of ionic conductors, the study of NMR linewidths or second moments as a function of pressure can also be used for the same purpose as is shown below. Assuming the motion of the mobile species to be a thermally activated process we have the dependence of ν_c , the jump frequency, on temperature given by the Arrhenius relation

$$\nu_c = \nu_0 \exp(-\Delta G/RT) \quad (3)$$

where ν_0 is the attempt frequency.

From the above relation we get the expression for activation volume as

$$\Delta V_M = (\partial \Delta G / \partial P)_T = -RT[(\partial \ln \nu_c / \partial P)_T - (\partial \ln \nu_0 / \partial P)_T]. \quad (4)$$

The pressure dependence of attempt frequency, $\partial \ln \nu_0 / \partial P$ can be estimated from Grüneisen parameter defined as $\gamma_G = -(\partial \ln \nu_0 / \partial \ln V)_T$ which can be written as $\gamma_G = -(\partial \ln \nu_0 / \partial P)_T (\partial P / \partial \ln V)_T$ or

$$(\partial \ln \nu_0 / \partial P)_T = -K_T \gamma_G \quad (5)$$

where K_T is the isothermal compressibility of the material given by the expression

$$K_T = (\partial \ln V / \partial P)_T. \quad (6)$$

Substituting $-K_T \gamma_G$ for $(\partial \ln \nu_0 / \partial P)_T$ in equation (4) we have

$$\Delta V_M = -RT[(\partial \ln \nu_c / \partial P)_T + K_T \gamma_G] \quad (7)$$

i.e.

$$\Delta V_M = RT[(\partial \ln \tau_c / \partial P)_T - K_T \gamma_G] \quad (8)$$

where $\tau_c \equiv 1/\nu_c$ is the correlation time. The value of τ_c at any pressure can be determined using the modified BPP formula (Vaughan *et al* 1972)

$$\tau_c = 2\pi \tan[\frac{1}{2}\pi(S - S_L)/(S_H - S_L)] / \alpha \gamma S^{1/2} \quad (9)$$

where S_H is the high-pressure second moment of the signal well above the transition pressure, S_L is the low-pressure motionally averaged second moment of the signal well below the transition pressure, S is the second moment at any intermediate pressure P , α is a constant usually taken to be equal to unity and γ is the gyromagnetic ratio of the resonant nucleus.

Since AFC undergoes a phase transition at around 0.45 GPa we use data below this pressure for the calculation of the activation volume. Figure 1 (inset) shows the plot of second moment against pressure at room temperature for the low-pressure phase from which the correlation times τ_c at different pressures were determined using equation

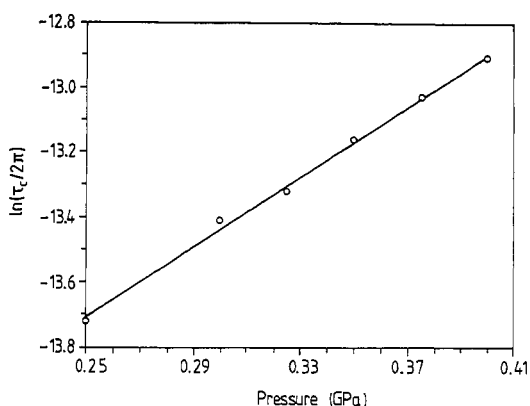


Figure 2. Pressure dependence of correlation time at room temperature.

(9). For the purpose of this calculation the value of S_H has been taken as $20.8 \times 10^{-3} \text{ mT}^2$ corresponding to the plateau region of figure 1 and S_L has been taken as $0.128 \times 10^{-3} \text{ mT}^2$. From the slope of the plot of $\ln \tau_c$ against P (figure 2) the value of the first term of eqn (8) turns out to be $13.63 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$.

The second term needs the values of the compressibility K_T and the Grüneisen parameter γ_G for its evaluation. We have earlier (Balasubramanyan *et al* 1988) measured the bulk modulus of AFC to be 11.65 GPa, from which one obtains $K_T = 8.5 \times 10^{-2} \text{ GPa}^{-1}$. The value of the Grüneisen parameter for AFC is not available at present. In the case of alkali halides, close to room temperature, γ_G varies from 1.45 for KCl to a maximum of 2 for CsBr (White 1965). Therefore, even if we put an upper limit of 5 for γ_G of AFC we see that $K_T \gamma_G \sim 0.425 \text{ GPa}^{-1}$ compared with $\partial \ln \tau_c / \partial P = 5.46 \text{ GPa}^{-1}$. Thus the second term of equation (8) is less than 10% of the first term and we shall ignore this term as has been done in other similar cases (e.g. Samara 1984, Matar *et al* 1980). Therefore the activation volume for AFC is $\Delta V_M \sim 13.63 \text{ cm}^3$. Taking the molar weight of $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 1.5\text{H}_2\text{O}$ to be 311.16 and the density to be 1.423 g cm^{-3} (Morosin 1978) the molar volume is found to be 218.6 cm^3 , and consequently the activation volume is found to be 6% of the molar volume.

The value of activation volume obtained from the study is considerably greater than those reported for other fast ion conductors (Samara 1984) and indicates a significant dilation of the lattice following ionic motion.

3.3. Activation energies

Temperature variation studies from room temperature down to 77 K were carried out at ambient pressure, 0.2 GPa, 0.3 GPa and 0.425 GPa. It was found that both at 0.2 GPa and 0.3 GPa there was only one signal throughout the temperature range 300–77 K with a continuous increase in linewidth with decrease in temperature of the sample. The lineshape comprising a narrow signal together with a broad signal was not observed at any temperature. By contrast, in the high pressure phase at 0.425 GPa, although there was only a single narrow signal from room temperature up to 260 K, a sudden change in lineshape was observed at 255 K with the appearance of a broad signal along with the narrow signal, the linewidth of the broad signal being 0.39 mT. With further lowering of sample temperature there was a rather steep increase in the linewidth of the narrow signal and finally at 210 K only a single broad signal was observed, indicating the complete freezing of the translational motion of all the mobile species in the compound.

Figure 3 shows the temperature dependence of linewidth at different pressures. An

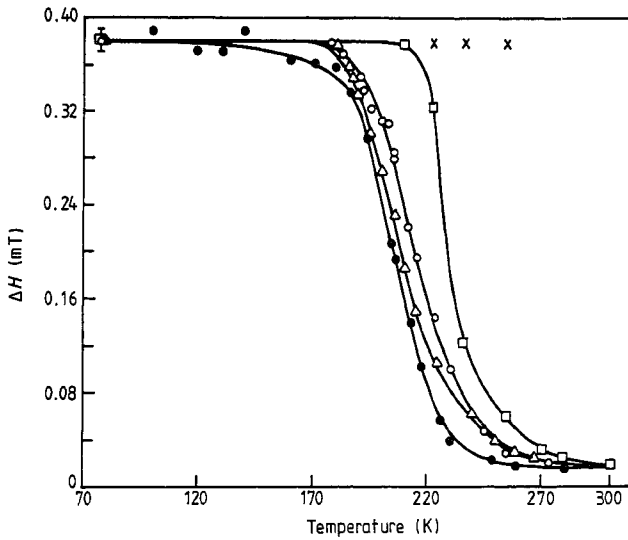


Figure 3. Temperature dependence of ^1H NMR linewidth at different pressures: ●, ambient; △, 0.2 GPa; ○, 0.3 GPa; □, 0.425 GPa (narrow signal); ×, 0.425 GPa (broad signal).

Table 1. Estimated values of E_a and ν_0 .

Pressure (GPa)	Activation energy E_a (kJ mol $^{-1}$)	Attempt frequency ν_0 (s $^{-1}$)
Ambient	16.25 ± 0.35	2.6×10^8
0.2	18.75 ± 0.48	8.24×10^8
0.3	20.46 ± 0.43	1.78×10^9
0.425	30.2 ± 1	1.38×10^{11}

examination of these plots reveals an increase in the temperature of line narrowing with increase in pressure indicating pressure effects on ionic motion. Using these plots the correlation frequencies at different temperatures in the region of line narrowing were calculated from the modified BPP formula (Gutowsky and Pake 1950),

$$\nu_c = \alpha\gamma\Delta H/2\pi \tan[\frac{1}{2}\pi(\Delta H^2 - B^2)/(A^2 - B^2)] \quad (10)$$

where A is the unnarrowed linewidth, B is the fully narrowed linewidth, ΔH is the measured linewidth at any temperature T in the region of narrowing and α is a numerical factor of order unity whose value depends on the lineshape. In AFC, as in other similar cases, the lineshape is lorentzian in the motionally narrowed region, gaussian in the rigid lattice regime and intermediate in the region of the transition. As a consequence, α is rather ill-defined and the use of equation (10) to determine the correlation frequencies in the transition region is only approximate even though far away from the transition it can be applied quite exactly. However, in practice, this equation is found to give results which are very close to those obtained by more accurate (and elaborate) methods (the results of which, to some extent, are model dependent) and is therefore preferred because of its great advantage of simplicity (Abragam 1961).

A plot of $\ln \nu_c$ against the inverse of temperature was made for each pressure and the activation energies (E_a) and attempt frequencies (ν_0) were estimated based on the Arrhenius relation. Figure 4 shows the Arrhenius plot obtained at 0.425 GPa. The estimated values of E_a and ν_0 are presented in table 1

In the low-pressure phase below 0.425 GPa there is a gradual increase in the values

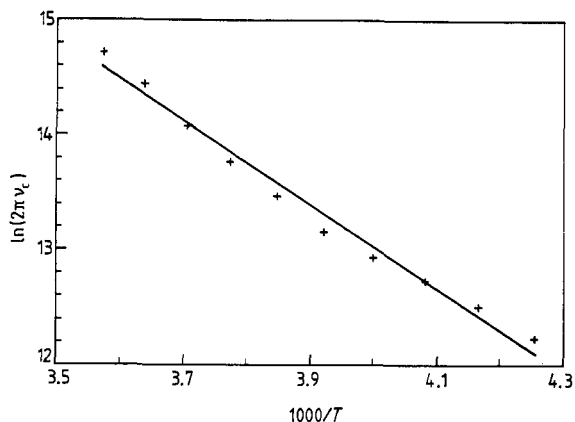


Figure 4. Arrhenius plot of jump frequency at 0.425 GPa.

of both activation energy and attempt frequency with increase in pressure. Similar effects have been observed previously in the high-pressure NMR study (Eguchi *et al* 1981) of lithium intercalation compound $\text{Li}_{0.94}\text{TiS}_2$. The transition to high-pressure phase at 0.425 GPa results in a steep increase in the values of E_a and ν_0 .

The variation of the second moment with pressure at 77 K is shown in figure 5. Whereas the linewidth (0.39 mT) remains unchanged as a function of pressure, the second moment registers a slight increase in the range 0.5 to 0.8 GPa. Recalling again that overall signal is made up of contributions from three different groups of protons, it can be concluded that at least one of the two ammonium groups is executing tunnelling reorientations so that the rigid lattice linewidth is not attained even by 1.5 GPa at 77 K. However, for the purposes of the present study we are not concerned with the tunnelling reorientations.

4. Conclusions

The activation volume of AFC reported here is the activation volume for motion in contrast to that for formation since the NMR results are sensitive to the motional correlation times. $\Delta V_M \sim 13.63 \text{ cm}^3 \text{ mol}^{-1}$ which we obtain for AFC is large in comparison with $\sim 2 \text{ cm}^3 \text{ mol}^{-1}$ reported for PbF_2 (Oberschmidt and Lazarus 1981) and PbSnF_4 (Matar *et al* 1980) and $\sim 0 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{H}_3\text{OUO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ (Kreuer *et al* 1983). Incidentally, $\text{H}_3\text{OUO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ appears to be the only protonic conductor for which activation volume has been measured apart from AFC reported in this paper. This large value rules out the possibility of the Grotthuss mechanism as the mode of ionic transport in AFC since Grotthuss mechanism consists of a succession of molecular reorientations

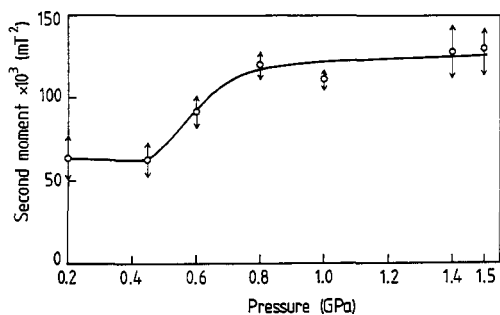


Figure 5. Pressure dependence of second moment at 77 K.

in AFC since Grotthus mechanism consists of a succession of molecular reorientations and proton jumps in a disordered hydrogen bond network and therefore is not very sensitive to pressure. This conclusion is also consistent with the structural study (Morosin 1978) which shows that in AFC, the distances involved are too large for the formation of hydrogen bonds. Normally, even for the vehicular mechanism which consists of co-operative motion of groups like H_3O^+ and H_2O one does not expect significant pressure effects. Therefore we infer that in AFC, the mechanism of translational motion is vacancy-assisted ionic jumping.

Another noteworthy feature of our results is the orders of magnitude lower pre-exponential factors (table 1) observed in AFC compared with the values of $\sim 10^{12}$ to 10^{13} Hz expected for typical attempt frequencies. In fact, this discrepancy is common to many of the fast ionic conductors. Either a breakdown of the absolute rate theory (Huberman and Boyce 1978) or low dimensionality effects (Richards 1978) are believed to be the cause of such discrepancies. Huberman and Boyce propose that when the mobile ions are much lighter than the rigid cage ions (a situation often realised in the case of protonic and lithium conductors), the interaction among them is not entirely inelastic and the energy transfer is not complete leading to the lower than expected attempt frequencies. The average energy transfer per collision is expected to increase with increasing pressure leading to an increase in the attempt frequencies with pressure. Our results (table 1) are consistent with this expectation and we believe therefore that our results support the breakdown of the absolute rate theory in the case of AFC. Further, AFC being a cubic crystal, the low-dimensionality effects cannot be very significant.

In conclusion, our high-pressure wide-line NMR studies at various temperatures indicate that vacancy-assisted ionic jump is the mechanism of charge transport in AFC.

Acknowledgments

We wish to thank Dr S Arumugam for the help rendered during the initial stages of this work. The research was supported by a project grant (DST/3/12/82-STP-III) to one of us (SVB).

References

- Abraham A 1961 *Principles of Nuclear Magnetism* (Oxford: Clarendon) p 456
- Andrew E R 1953 *Phys. Rev.* **91** 425
- Balasubramanyan D R and Bhat S V 1987 *Solid State Ionics* **23** 267
- Balasubramanyan D R, Bhat S V, Mohan M and Singh A K 1988 *Solid State Ionics* **28-30** 664
- Eguchi T, Marinos C and Jonas J 1981 *Solid State Commun.* **38** 919
- Gutowsky H S and Pake G E 1950 *J. Chem. Phys.* **18** 162
- Huberman B A and Boyce J B 1978 *Solid State Commun.* **25** 759, 843
- Kreuer K D, Stoll I and Rabenau A 1983 *Solid State Ionics* **9 & 10** 1061
- Matar S, Reau J M, Demazeau G, Lucat C, Portier J and Hagemuller P 1980 *Solid State Commun.* **35** 681
- Morosin B 1978 *Acta Cryst. B* **34** 3730
- Oberschmidt J and Lazarus D 1980 *Phys. Rev. B* **21** 2952
- Ramanathan K V and Srinivasan R 1978 *J. Phys. Chem. Solids* **39** 891
- Richards P M 1978 *Solid State Commun.* **25** 1019
- Samara G A 1984 *Solid State Physics* vol 38, ed. H Ehrenreich and D Turnbull (New York: Academic)
- Vaughan R W, Nicolaides G L and Elleman D D 1972 *J. Chem. Phys.* **56** 4480
- White G K 1965 *Proc. R. Soc. A* **286** 204
- Whittingham M S, Connell P S and Huggins R A 1972 *J. Solid State Chem.* **5** 321