

- ARIYA, S. M. & GOLOMOLZINA, M. V. (1962). *Fiz. Tverd. Tela (Leningrad)*, **4**, 2921–2924.
- BANUS, M. D. & REED, T. B. (1970). *The Chemistry of Extended Defects in Non-Metallic Solids*, edited by L. EYRING & M. O'KEEFE, pp. 488–522. Amsterdam: North-Holland.
- BANUS, M. D., REED, T. B. & STRAUSS, A. J. (1972). *Phys. Rev. B*, **5**, 2775–2784.
- BATTERMAN, B. W., CHIPMAN, D. R. & DEMARCO, J. J. (1961). *Phys. Rev.* **122**, 68–74.
- BORIE, B. & SPARKS, C. J. (1971). *Acta Cryst.* **A27**, 198–201.
- CROMER, D. T. (1969). *J. Chem. Phys.* **50**, 4857–4859.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- GEHLEN, P. C. & COHEN, J. B. (1965). *Phys. Rev. A*, **139**, 844–855.
- GOODENOUGH, J. B. (1972). *Phys. Rev. B*, **5**, 2764–2774.
- GOODENOUGH, J. B. (1973). *Defects and Transport in Oxides*, edited by M. S. SELTZER & R. I. JAFFEE, pp. 55–82. New York: Plenum.
- GRAGG, J. E. JR (1970). PhD Thesis, Northwestern Univ., Evanston, Illinois 60201.
- GRAGG, J. E. JR & COHEN, J. B. (1971). *Acta Metall.* **19**, 507–519.
- HAYAKAWA, M. & COHEN, J. B. (1975). *Acta Cryst.* **A31**, 635–645.
- HAYAKAWA, M., MORINAGA, M. & COHEN, J. B. (1973). *Defects and Transport in Oxides*, edited by M. S. SELTZER & R. I. JAFFEE, pp. 177–199. New York: Plenum.
- HÖIER, R. & ANDERSSON, B. (1974). *Acta Cryst.* **A30**, 93–95.
- HORIUCHI, H., MORIMOTO, N. & TOKONAMI, M. (1976). *J. Solid State Chem.* **17**, 407–424.
- HUANG, K. (1947). *Proc. R. Soc. London Ser. A*, **190**, 102–116.
- IIDA, S. (1955). *Progress of Magnetism*, edited by S. CHIKAZUMI, pp. 292–301 (in Japanese). Tokyo: Agne.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KAWANO, S., KOSUGE, K. & KACHI, S. (1966). *J. Phys. Soc. Jpn*, **21**, 2744–2745.
- KOCH, F. & COHEN, J. B. (1969). *Acta Cryst.* **B25**, 275–287.
- KOMATSU, K. & TERAMOTO, K. (1966). *J. Phys. Soc. Jpn*, **21**, 1152–1159.
- MORINAGA, M. (1978). PhD Thesis, Northwestern Univ., Evanston, Illinois 60201.
- MORINAGA, M. & COHEN, J. B. (1976). *Acta Cryst.* **A32**, 387–395.
- MORINAGA, M. & COHEN, J. B. (1979). *Acta Cryst.* **A35**, 745–756.
- SCHÖNBERG, N. (1954). *Acta Chem. Scand.* **8**, 221–225.
- SCHWARTZ, L. H. & COHEN, J. B. (1977). *Diffraction from Materials*. New York: Academic Press.
- SCHWARTZ, L. H., MORRISON, L. A. & COHEN, J. B. (1963). *Adv. X-ray Anal.* **7**, 281–301.
- STENSTRÖM, G. & WESTMAN, S. (1968). *Acta Chem. Scand.* **22**, 1712–1714.
- SWALIN, R. A. (1961). *Thermodynamics in Solids*. New York: Wiley-Interscience.
- TERAUCHI, H. & COHEN, J. B. (1979). *Acta Cryst.* **A35**, 646–652.
- TERAUCHI, H., COHEN, J. B. & REED, T. B. (1978). *Acta Cryst.* **A34**, 556–561.
- WATANABE, D., ANDERSSON, B., GJÖNNES, J. & TERASAKI, O. (1974). *Acta Cryst.* **A30**, 772–776.
- WATANABE, D., CASTLES, J. R., JOSTSONS, A. & MALIN, A. S. (1967). *Acta Cryst.* **A23**, 307–313.
- WESTMAN, S. & NORDMARK, C. (1960). *Acta Chem. Scand.* **14**, 465–470.
- WILLIAMS, R. O. (1972). Report ORNL-4828. Oak Ridge National Laboratory, Tennessee.
- WOLFF, P. M. DE (1956). *Acta Cryst.* **9**, 682–683.
- WOLLAN, E. O. (1960). *Phys. Rev.* **117**, 387–401.
- Acta Cryst.* (1979). **A35**, 989–991

## The Interpretation of Neutron Powder Diffraction Measurements on $\alpha$ -AgI

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### Abstract

Recent neutron powder diffraction measurements on  $\alpha$ -AgI by Wright & Fender [*J. Phys. C* (1977), **10**, 2261–2267] have been reanalysed using conventional least-squares analysis of the integrated Bragg intensities and have been shown to be consistent with other recent

neutron diffraction measurements and with recent extended X-ray absorption fine structure (EXAFS) measurements. It is concluded that, although the distribution of silver ions within the unit cell can be modelled by locating isotropically vibrating ions in a number of crystallographic sites with partial occupancy, the most appropriate model is one in which the silver ions are located entirely in a single site but

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have significant anisotropic harmonic and higher-order components in their thermal vibration.

### Introduction

The structure of  $\alpha$ -AgI is of particular interest because of its superionic conductivity, but until recently diffraction studies of this material have been restricted to powder samples because of the difficulty of preparing single crystals. As a consequence of the large temperature factors, particularly for the silver ions, the number of Bragg intensities which can be determined from a powder diffraction study is severely limited and a number of different 'static' models have been proposed for the distribution of silver ions in the unit cell (see, for example, Stroock, 1934, 1936; Hoshino, 1957; Bührer & Hälg, 1974; Wright & Fender, 1977). These models consider the silver ions to be distributed over a number of possible sites with isotropic harmonic thermal vibrations. However, recent extended X-ray absorption fine structure (EXAFS) measurements by Boyce, Hayes, Stutius & Mikkelsen (1977) have proved to be inconsistent with these proposed models, since they indicate that the silver-ion distribution is best accounted for by a jump-diffusion model. Hoshino, Sakuma & Fujii (1977) have therefore analysed new neutron powder diffraction data for  $\alpha$ -AgI and concluded that both these and the earlier X-ray data of Hoshino (1957) are well explained by a model, consistent with the EXAFS results, in which the silver-ion distribution is described in terms of a single tetrahedrally coordinated equilibrium site with appreciable harmonic and higher-order anisotropic components in the thermal vibrations. Also, following successful nucleation of single crystals, Cava, Reidinger & Wuensch (1977) have recently carried out a single-crystal neutron diffraction study of  $\alpha$ -AgI in which they were able to use a similar model. Support for such a model is also provided by a molecular-dynamics study by Vashista & Rahman (1978).

### Neutron powder diffraction data

Apart from that of Hoshino *et al.* (1977), the most recent powder diffraction study of  $\alpha$ -AgI is that of Wright & Fender (1977), also using neutrons. These authors analysed their data using the profile refinement method, developed originally by Rietveld (1969), which we have since shown gives incorrect results for these data (Sakata & Cooper, 1979). The main criticism of this method arises because the standard deviations of the parameters are calculated incorrectly. However, its usefulness for this type of problem is also restricted, since it is not easy to introduce higher-order cumulants into the structural model. Since the diffraction pattern

in this case consists of a number of well resolved peaks, there is no reason why a more appropriate analysis based on the integrated intensities cannot be carried out. Wright & Fender published the necessary integrated intensity data for their measurements at 453 K and we have therefore analysed these using a conventional refinement method, capable of including higher-order cumulants in the model.

The structure of  $\alpha$ -AgI is based on the space group  $Im\bar{3}m$  and, with the iodine ions located at the  $2(a)$  sites  $(0,0,0)$ , the possible sites which have been considered for the silver ions are:  $6(b)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ ;  $12(d)$ ,  $(\frac{1}{4}, 0, \frac{1}{2})$ ;  $24(g)$ ,  $(x, 0, \frac{1}{2})$  and  $24(h)$ ,  $(x, x, 0)$ , with the two silver ions distributed over the sites appropriate to each particular model. The location of these sites is illustrated in Fig. 1. Although the  $12(d)$  site is the only reasonable single site, other models have been proposed in order to account for the inadequacy of the  $12(d)$  model on its own if isotropic harmonic thermal vibrations are assumed. In particular, the  $24(g)$  model, which corresponds to a splitting of the  $12(d)$  site with a displacement along the  $x$  axis, allows for anisotropy in the harmonic thermal vibrations of the ions in the  $12(d)$  site and inclusion of the  $6(b)$  and  $24(h)$  sites with the  $12(d)$  site, as for example in the Stroock model, may allow for other anisotropic features.

Wright & Fender (1977) analysed their data on the basis of six models, including the Stroock model and models with isotropic (harmonic) silver ions in each of the four possible sites separately. Only the  $12(d)$  and  $24(g)$  models gave reasonable results. We have reanalysed their data with conventional integrated intensity refinement using the Harwell *TAILS* program. The  $12(d)$  and  $24(g)$  models gave results similar to those obtained by Wright & Fender, with  $R(I)$  values of 8.3 and 4.7% respectively, although different values were obtained for the derived parameters and their

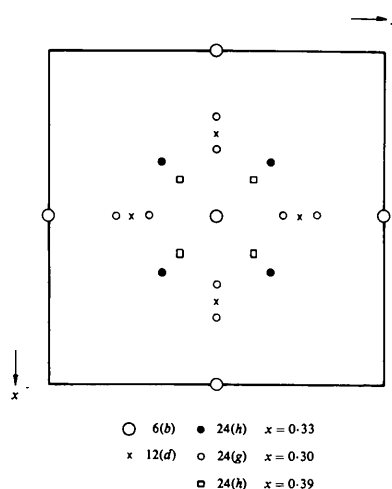


Fig. 1. Distribution of possible Ag sites within the (001) face of the unit cell. I ions are located at the corners of the face.

standard deviations (see Table 1 and Sakata & Cooper, 1979).

The 24(g) model and the inclusion of the 6(b) sites in the Strock model both simulate increased thermal vibration of the ion in the 12(d) site at  $(\frac{1}{2}, 0, \frac{1}{2})$  along the  $x$  axis. The inclusion of the 24(h) site in the Strock model simulates a further increase of the thermal vibration of the ion in the 12(d) site towards neighbouring 12(d) sites. Analysis of the powder data in terms of a model with the majority of the silver ions located in the 12(d) sites but with an additional partial occupancy of a 24(h) 'window' site gave an  $R(I)$  value of 3.1%, with a value of  $x = 0.385$  (7) and a site occupancy of 0.84 (23). This is therefore a better model for the powder data.

Because of the larger number of reflections available in the single-crystal data Cava, Reidinger & Wuensch were able to analyse their results in terms of an anharmonic model, in which the silver ions are located only at the 12(d) sites, but several higher-order anharmonic terms are included in the representation of their thermal motion. This model has 11 parameters, so that even for the single-crystal analysis the number of data is little more than twice the number of parameters, but since there are only 9 powder data it is clearly out of the question to use such a complex model for the latter. However, we have nevertheless considered the more significant thermal parameters in order to test the consistency of the two sets of data.

Introduction of anisotropy for the harmonic  $B$  factor for silver, with  $B_{22} = B_{33} \neq B_{11}$  and all other  $B_{ij} = 0$ , gave a reduction in the  $R(I)$  value from 8.3% for the isotropic 12(d) model to 4.6%, with  $B_{11}$  significantly larger than  $B_{22}$ , corresponding to an increased vibration in the direction of the 24(g) sites. Subsequent intro-

duction of a third-order term  $C_{122} = -C_{133}$ , with all other  $C_{ijk} = 0$ , led to a further reduction in  $R(I)$  to 2.8%. Because of the limited number of data fourth-order terms could only be introduced with the other thermal parameters fixed and no significant improvement resulted from their inclusion. However, it was clear that effects due to fourth-order terms were much less than those due to third-order terms, being smaller than the standard deviations of the observed data. Thus the powder diffraction data are not able to provide evidence for the existence of significant fourth-order terms in the thermal vibrations.

## Conclusions

The results of our analysis are summarized in Table 1. Within their limitations the neutron powder data of Wright & Fender (1977) are clearly entirely consistent with the conclusions of Hoshino, Sakuma & Fujii (1977) and with the EXAFS results of Boyce, Hayes, Stutius & Mikkelsen (1977). As is also the case for the single-crystal data of Cava, Reidinger & Wuensch (1977), the best model for the powder data is that in which the silver ions are located only in the 12(d) sites but have anisotropic harmonic and higher-order components in their thermal vibrations. This model thus accounts for the main features of the silver-ion distribution, which can only be approximated by the multi-site 'static' models. However, the limitations of the powder data are such that the improvement over the best 'static' model is not statistically significant at the 0.5% level (see Hamilton, 1965). Although fourth-order terms were derived for the single-crystal data, it must be emphasized that in all these analyses the number of observations is only about twice the number of parameters and the results must therefore be considered with some caution.

Table 1. Summary of results obtained from the analyses

Sites	Model				
	12(d)	24(g)	12(d) 24(h)	12(d)	12(d)
Temperature factors*	$B_i$	$B_i$	$B_i$	$B_a$	$B_a, C_a$
$B_i$ ( $\text{\AA}^2$ )	7.8	7.8	7.5	7.8	7.8
$\sigma(B_i)$	0.9	0.5	0.5	0.5	—
$(B_{11})_{AG}$ ( $\text{\AA}^2$ )	12.4	11.5	8.8	16.5	18.8
$\sigma(B_{11})$	2.1	1.3	1.6	1.7	1.6
$(B_{22})_{AG}$ ( $\text{\AA}^2$ )	$= B_{11}$	$= B_{11}$	$= B_{11}$	11.2	12.2
$\sigma(B_{22})$				1.4	1.0
$(C_{122})_{AG}$ ( $\text{\AA}^3$ )	0	0	0	0	7.3
$\sigma(C_{122})$					3.2
$x$		0.299	0.385		
$\sigma(x)$		0.007	0.007		
$n_2^\dagger$			0.84		
$\sigma(n_2)$			0.23		
$R(I)$ (%)	8.3	4.7	3.1	4.6	2.8

\*  $i$  = isotropic,  $a$  = anisotropic.

†  $n_2$  = occupation of 24(h) site.

## References

- BOYCE, J. B., HAYES, T. M., STUTIUS, W. & MIKKELSEN, J. C. (1977). *Phys. Rev. Lett.* **38**, 1362–1365.  
 BÜHRER, W. & HÄLG, W. (1974). *Helv. Phys. Acta*, **47**, 27.  
 CAVA, R. J., REIDINGER, F. & WUENSCH, B. J. (1977). *Solid State Commun.* **24**, 411–416.  
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.  
 HOSHINO, S. (1957). *J. Phys. Soc. Jpn.*, **12**, 315–326.  
 HOSHINO, S., SAKUMA, T. & FUJII, Y. (1977). *Solid State Commun.* **22**, 763–765.  
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.  
 SAKATA, M. & COOPER, M. J. (1979). *J. Appl. Cryst.* **12**. In the press.  
 STROCK, L. W. (1934). *Z. Phys. Chem. Abt. B*, **25**, 441.  
 STROCK, L. W. (1936). *Z. Phys. Chem. Abt. B*, **31**, 132.  
 VASHISTA, P. & RAHMAN, A. (1978). *Phys. Rev. Lett.* **40**, 1337–1340.  
 WRIGHT, A. F. & FENDER, B. E. F. (1977). *J. Phys. C*, **10**, 2261–2267.