Acta Cryst. (1979). B**35**, 1538–1539

Differences between diffraction and vibrational spectroscopic results for $\mathrm{AgNO_3}$.

By M. H. Brooker,
Department of Chemistry, Memorial University of Newfoundland, St John's, Newfoundland A1B 3X7, Canada

(*Received* 27 *January* 1979; *accepted* 27 *March* 1979)

Abstract

The infrared and Raman spectra of $\mathrm{AgNO_3}$ are more consistent with the old *Pbca* structure than with the newly proposed $P2_12_12_1$. The nature of the problem is discussed and it is concluded that basic differences between the spectroscopic and diffraction methods may account for the discrepancy.

Recently Meyer, Rimsky & Chevalier (1978, hereafter MRC) have reported $\mathrm{AgNO_3}$ to have the noncentrosymmetric space group $P2_12_12_1$. However, results from infrared and Raman spectroscopic studies are not in agreement with this proposal (Huang & Brooker, 1976). It is the object of the present communication to describe the nature of the differences and to present possible reasons for the discrepancies, since the problem appears to indicate a basic limitation in one or both techniques. Similar ambiguities have been reported for $\mathrm{Ba(NO_3)_2}$ (Brooker, 1979; Brooker & Bates, 1973). In this case Raman and infrared studies indicated the centrosymmetric structure *Pa*3, whereas neutron studies (Birnstock, 1967) suggested the noncentrosymmetric $P2_13$. Recently Weber & Haussühl (1977) have reported that even with the aid of highly sensitive methods, no piezoelectric, linear electro-optic and non-linear optic effects, and also no optical activity could be detected in $\mathrm{Sr(NO_3)_2}$, $\mathrm{Ba(NO_3)_2}$ and $\mathrm{Pb(NO_3)_2}$: results which are only compatible with point symmetry *m*3 for these crystals, consistent with the spectroscopic analysis.

The problem for both $\mathrm{AgNO_3}$ and $\mathrm{Ba(NO_3)_2}$ centres on the presence or absence of a centre of symmetry, the long-standing problem of X-ray analysis. MRC presented convincing evidence on the basis of an analysis of over 4000 reflections that the true space group for $\mathrm{AgNO_3}$ was the noncentrosymmetric $P2_12_12_1$ as proposed by Niggli (1959). In support of this claim they have confirmed the morphologic studies of Zachariasen (1928) and Niggli (1959), both of whom reported the crystal class as 222. Lindley & Woodward (1966, hereafter LW) had reported the complete structure of $\mathrm{AgNO_3}$ based on the centrosymmetric space group *Pbca* and Trotter & Gibbons (1971, hereafter TG) confirmed this structure in a more accurate study. Both the LW and the MRC structures place the eight $\mathrm{NO_3^-}$ groups on general positions but there is a major difference in that the MRC structure has *two sets* of non-equivalent $\mathrm{NO_3^-}$ groups. In the LW structure all eight $\mathrm{NO_3^-}$ groups are equivalent. It is worth pointing out that there are some rather significant differences in the N–O lengths between the two reported structures (MRC and TG).

Recently we have reported a detailed analysis of the infrared and Raman spectra of single-crystal $\mathrm{AgNO_3}$ over a wide range of temperatures (Huang & Brooker, 1976). Our conclusions were that the results were in excellent agreement with the LW structure. Three separate pieces of data were in accord with the centrosymmetric structure. (*a*) Lack of coincidence between certain infrared and Raman peaks was detected. This was most convincing in the ν_4 region where all eight predicted Raman active components were observed at 711·5, 712·0, 714·4, 715·1, 731·8, 737·2, 732·6 and 734·4 cm^{-1} and, although some infrared peaks showed near-coincidence, one peak at 728·9 cm^{-1} was clearly not coincident. (*b*) A search of the ν_3 region of the Raman spectrum on powders and single crystals of appropriate orientation failed to reveal any evidence for a longitudinal optical (LO) mode which has been detected in the infrared polarized specular reflection spectrum at 1410 cm^{-1} (Bates & Brooker, 1973). None of the Raman peaks in the ν_3 region showed anomalous frequency changes with change in scattering angle which would also be characteristic of an LO mode. LO modes are theoretically allowed for noncentrosymmetric crystals and have been observed for $\mathrm{NaClO_3}$ (Hartwig, Rousseau & Porto, 1969) and $\mathrm{NaNO_2}$ (Asawa & Barnoski, 1970). (*c*) Perhaps most important was the failure to detect evidence for the non-equivalent $\mathrm{NO_3^-}$ groups. Raman spectra of $\mathrm{AgNO_3}$ at 77 K recorded at slightly better than 1·0 cm^{-1} resolution (0·25 cm^{-1} slits) showed only a single sharp peak at 1046·9 cm^{-1} for the modes with symmetric scattering tensors which indicated that only one distinguishable family of $\mathrm{NO_3^-}$ groups was present. A careful study of the $\mathrm{N^{18}O^{16}O_2^-}$ peak at 1026·3 cm^{-1} also revealed only a single sharp peak. This peak is uncoupled from the lattice and is even more diagnostic of the number of families than the $\mathrm{N^{16}O_3^-}$ peak which is coupled to the ordered lattice. For $\mathrm{RbNO_3}$ and $\mathrm{CsNO_3}$ which have been shown to have three families of $\mathrm{NO_3^-}$ groups, three peaks *have* been detected in the symmetric stretching region (Brooker, 1973). Similarly for $\mathrm{TlNO_3}$ which has two non-equivalent sets of $\mathrm{NO_3^-}$ groups a doubling of peaks has been detected (Pogarev & Shultin, 1973; Brooker & Huang, 1975). Basically the arguments quoted for the infrared and Raman support of the centrosymmetric structure of $\mathrm{AgNO_3}$ are identical to those which supported the centrosymmetric structure of $\mathrm{Ba(NO_3)_2}$ and a more detailed discussion and references can be found in Brooker (1979) and Brooker & Bates (1973).

Several rather basic questions come to mind. Are the infrared and Raman or X-ray data treatments experimentally poor? Are the infrared and Raman results insensitive to small departures from centrosymmetry? Are there basic differences between the spectroscopic and diffraction techniques which can account for the apparent discrepancy? The answer to the first question is a hesitant no, but it remains for future workers to check the fundamental accuracy and treatment of the data. The second question can be answered with a perhaps, but in other cases the spectroscopic methods have not been shown to be so

0567-7408/79/061538-02$01.00

limited. There are basic differences between the two methods which could account for the discord and these will be discussed.

The perfect* crystal does not exist. Just as the bilateral symmetry of the human body does not stand up to close scrutiny neither does the normal crystal. For instance in a crystal of $AgNO_3$ 4·9% of the unit cells will contain an ^{18}O atom, 3·0% an ^{15}N atom, while the isotopes of ^{107}Ag and ^{190}Ag are 51·8 and 48·2% abundant. If added to this are packing faults, defects, strains and anharmonic factors the crystal is far from perfect and the concept of symmetry becomes less precise. It does appear that infrared and Raman spectroscopy can occasionally differentiate between the ordered and the disordered parts of the lattice. Typically vibrational spectroscopy detects the normal modes near the zone centre ($k \simeq 0$) which are the in-phase motions of coupled unit cells. Both substitutional and anharmonic shallow-well defect centres may be incorporated into the ordered spectrum for certain modes but deep-well defects will be decoupled from the ordered lattice and appear as local modes (Belousov, Pogarev & Shultin, 1977; Brooker, 1979). Usually the local modes are not included in the vibrational analysis and symmetry arguments are based only on the ordered part of the spectrum. In a diffraction analysis all atoms are included and small discrepancies probably appear in the thermal parameters. Some of the problems associated with treating thermal motions of atoms have been discussed by Willis & Pryor (1975). They point out that anharmonic effects can cause mean-square displacements to be anisotropic as well as giving rise to the appearance of theoretically forbidden reflections. Since the root-mean-square rotation of the plane of the NO_3^- groups in $AgNO_3$ may be as great as 8° at room temperature (TG) it is difficult to envisage the atomic positions being placed with a high degree of certainty. MRC employed only isotropic thermal factors for the N and O atoms and it is possible that these do not adequately account for the large thermal motions. Careful low-temperature diffraction data would provide useful information on the anharmonic motions in $AgNO_3$ and could perhaps help resolve the $AgNO_3$ structure problem.

---

* The use of the word perfect employed here does not appear to be the same as that used by MCR.

References

ASAWA, C. K. & BARNOSKI, M. K. (1970). *Phys. Rev. B*, **2**, 205–213.

BATES, J. B. & BROOKER, M. H. (1973). *Chem. Phys. Lett.* **21**, 349–353.

BELOUSOV, M. V., POGAREV, D. E. & SHULTIN, A. A. (1977). *Phys. Status Solidi B*, **80**, 417–424.

BIRNSTOCK, R. (1967). *Z. Kristallogr.* **124**, 310–334.

BROOKER, M. H. (1973). *J. Chem. Phys.* **59**, 5828–5829.

BROOKER, M. H. (1979). *J. Solid State Chem.* In the press.

BROOKER, M. H. & BATES, J. B. (1973). *Spectrochim. Acta Part A*, **29**, 439–452.

BROOKER, M. H. & HUANG, C.-H. (1975). Paper presented at the 22nd Spectroscopy Society of Canada Symposium, Montreal, Canada.

HARTWIG, C. M., ROUSSEAU, D. L. & PORTO, S. P. S. (1969). *Phys. Rev.* **188**, 1328–1335.

HUANG, C.-H. & BROOKER, M. H. (1976). *Spectrochim. Acta Part A*, **32**, 1715–1724.

LINDLEY, P. F. & WOODWARD, P. (1966). *J. Chem. Soc. A*, pp. 123–126.

MEYER, P., RIMSKY, A. & CHEVALIER, R. (1978). *Acta Cryst.* B**34**, 1457–1462.

NIGGLI, A. (1959). *Z. Kristallogr.* **111**, 269–282.

POGAREV, D. E. & SHULTIN, A. A. (1973). *Kristallografiya*, **18**, 311–314.

TROTTER, J. & GIBBONS, C. S. (1971). *J. Chem. Soc. A*, pp. 2058–2062.

WEBER, H.-J. & HAUSSÜHL, S. (1977). *Z. Kristallogr.* **146**, 303–307.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 142–174. Cambridge Univ. Press.

ZACHARIASEN, W. (1928). *Untersuchung über die Kristallstrukturen von Sesquioxyden und Verbindungen ABO_3. Partie* 4. Oslo: Skrifter.

International Union of Crystallography

Acta Cryst. (1979). B**35**, 1539

Structure Reports

Volumes 43A and 42B of *Structure Reports* have recently been published. Volume 43A, covering the literature for metals and inorganic compounds for 1977 (vi + 393 pages), costs 97·75 Netherlands guilders for subscribers with standing orders. The full price for individual copies is 115 guilders but personal subscribers may buy a copy for their own use at 57.50 guilders.

Volume 42B, covering the literature for organic compounds for 1976, is bound in two parts (vi + 506 pages and iv + 625 pages) and costs 272 Netherlands guilders for subscribers with standing orders. The full price for individual copies is 320 guilders but personal subscribers may buy a copy for their own use at 160 guilders.

Orders for these publications may be placed direct with the publisher, Bohn, Scheltema & Holkema, PO Box 23, 7400 GA Deventer, The Netherlands, with Polycrystal Book Service, PO Box 11567, Pittsburgh, PA 15238, USA, or with any bookseller.