Is Cerussite an Aragonite? Longitudinal Optical–Transverse Optical Splitting in the Single-crystal Raman Spectra

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Single-crystal Raman studies on cerussite, $PbCO_3$, show longitudinal optical–transverse optical splitting effects and are incompatible with this material having the aragonite lattice; a $Pna2_1$, C_{2v}^{9} structure is indicated.

The crystal structure of the mineral cerussite, $PbCO_3$, has been the subject of debate for more than two decades. It has been recognised that its i.r. spectral frequencies do not mirror the patterns set by other aragonite ($Pnma$, D_{2h}^{16}) minerals,[1–3] but it is only recently that the vibrational spectra of these minerals have been understood,[4,5] and it has become possible to reconsider the cerussite problem. Its reported crystal structure[6,7] is such that it would be expected to conform the closest to the 'near D_{3d}^{3} ($P\bar{3}m1$)' model for the vibrational spectra of aragonite materials. Instead, its polycrystalline Raman spectrum (Figure 1), even more than its i.r. spectrum, shows anomalous peak occurrences and intensities both for material from geological sources and for synthetic cerussite. We have therefore investigated this aspect of the problem by a single-crystal Raman study.

Conventionally, one indication of the absence of a crystallographic centre of symmetry has been taken to be the appearance of coincidences between i.r. and Raman frequencies of the crystalline materials.[†] However, this has proved an unreliable criterion for two reasons. First, a small deviation from a centrosymmetric structure does not immediately produce i.r.–Raman coincidences since, for example, the polarizability changes in the i.r.-active modes might not be enough to produce appreciable Raman intensity and secondly, coincidences occur on modes amenable to the site group model (unless the site is itself centrosymmetric) for here the existence of a crystallographic centre of symmetry is irrelevant. However, single-crystal Raman spectra enable a clear distinction between centrosymmetric and non-centrosymmetric lattices, since longitudinal optical–transverse optical effects may be observed notwithstanding the absence of i.r. and Raman coincidences.

A structure with C_{2v}^{9} ($Pna2_1$) symmetry, which like the aragonite structure is a small distortion from D_{3d}^{3}, lacks the centre of symmetry present in D_{3d}^{3} and, immediately and discontinuously, a polar character is permitted in the Raman-active vibrational modes. Consequently, long range dipolar coupling effects may appear, as a separation of longitudinal (L.O.) and transverse (T.O.) components, in the Raman and mean that the spectral predictions for a C_{2v}^{9} lattice do not reduce to those for a near-D_{3d}^{3} model. Such long-range dipolar splittings can be large in simple materials, for example a value of *ca.* 200 cm^{-1} has been reported for ZnO,[8] and *ca.* 150 cm^{-1} for carbonates with the calcite structure,[9] so that the introduction of only a small amount of polar character is required for a splitting of a few wavenumbers to be observed, unless the peaks are unusually broad. L.O.–T.O. effects are always of relevance in i.r. spectra, irrespective of the presence or absence of a crystallographic centre of symmetry, and so it is understandable that the i.r. spectrum of cerussite is not grossly dissimilar from those of materials with the aragonite lattice. As an example of the occurrence of L.O.–T.O. splittings in the internal-mode Raman spectra of cerussite, in Figure 2 we give the $x(zx)z$ and $y(xz)\bar{y}$ spectra. For a centrosymmetric space group these two spectra should be essentially identical. In a non-centrosymmetric space group they differ because of the different pattern of (z-directed) dipoles (L.O.–T.O. splitting). The clear differences seen in Figure 2 are reproducible and not caused by mis-setting. They are consistent only with a non-centric space group and we conclude that cerussite does not have the $Pnma$ (D_{2h}^{16}) lattice but, rather $Pna2_1$ (C_{2v}^{9}). This conclusion is consistent not only with a detailed analysis of the L.O.–T.O. splittings we observe but also with the more

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[†] A material crystallizing in a non-centric space group should also show a piezoelectric effect, but none has been detected for cerussite, although with the apparatus available to us a small effect would have gone undetected.

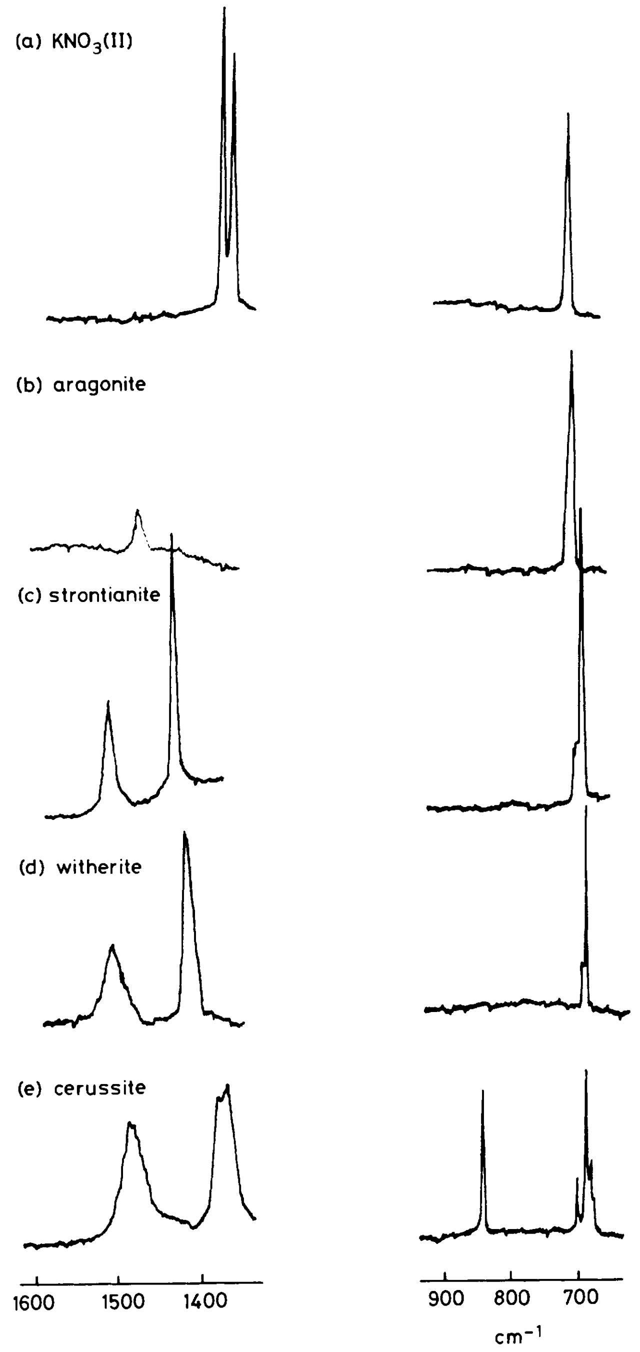

Figure 1. Raman spectra of the internal mode regions of polycrystalline samples of aragonite minerals (a—d) and cerussite (e). Single crystal studies[10] show a peak at 1574 cm^{-1} in aragonite, a component of the asymmetric stretch not observed in our polycrystalline study owing to the fluorescent nature of the available sample. Frequencies are accurate to ±2 cm^{-1}.

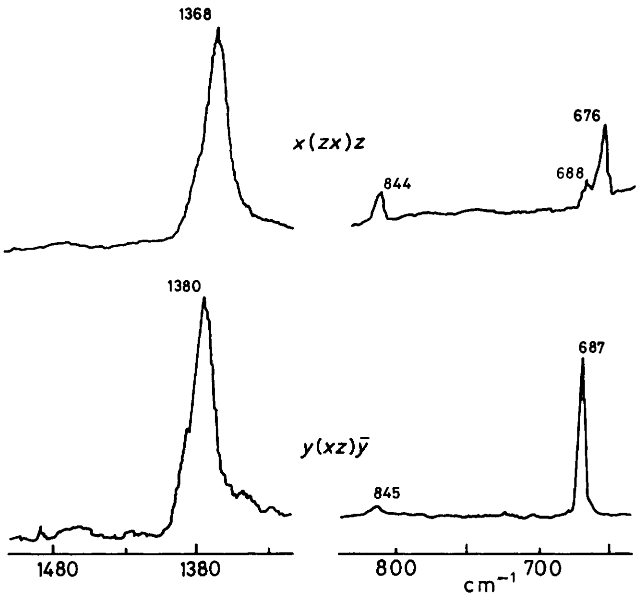

Figure 2. L.O.-T.O. splitting in the 1400 and 680 cm^{-1} bands of cerussite. This splitting explains the double-headed nature of the *ca.* 1370 cm^{-1} peak in Figure 1 and, in part, the multiplicity in the 690 cm^{-1} region.

routine aspects of the single-crystal Raman study which, independently, are inconsistent with the *Pnma* space group (see, for example, the peak at 844 cm^{-1}, unique to cerrusite). The single-crystal Raman spectra of witherite ($BaCO_3$), the most similar genuine aragonite species, show none of the complexities exhibited by $PbCO_3$.

We conclude that, notwithstanding the crystallographic evidence to the contrary, cerussite does not have the aragonite lattice but, rather exhibits a distortion, presumably in the arrangement of carbonate anions, which removes the centre of symmetry and leads to a $Pna2_1(C^9_{2v})$ lattice. The crystal structure of cerussite is being reinvestigated in the hope of removing the discrepancy which now exists between crystallographic and spectroscopic data,[11] although this may not be possible using *X*-ray methods alone.[12]‡

We are indebted to the British Museum (Natural History) for supplying the samples used in this work and Dr. C. Kellsey of the Department of Earth Science, University of Cambridge, for the measurements of piezoelectricity.

Received, 18th February 1985; Com. 203

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‡ We have refined the published *X*-ray data[7] in both *Pnma* and $Pna2_1$, although we were unable to correct properly for absorption. Identical *R* values were obtained (7.3%).