

# ON THE STRUCTURE OF AMETHYST AND ITS GENESIS IN NATURE

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Received December 14, 1954

## 1. INTRODUCTION

IN a recent issue of these *Proceedings*,<sup>1</sup> evidence was presented showing that amethyst is a crystalline solid akin to colourless quartz in its structure but with a different electronic configuration which is assignable to a lower symmetry class and giving X-ray reflection intensities differing from those of quartz. These findings are supported and illumined by the results reported in a paper by S. Pancharatnam<sup>2</sup> published simultaneously with ours. It was shown by him that amethyst is optically biaxial and exhibits trichroism, and that when these two properties are considered together, they indicate only monoclinic symmetry for amethyst, whereas colourless quartz has trigonal symmetry. Interesting relationships however exist between amethyst and the associated quartz in their crystallographic orientations. The monoclinic symmetry axis of amethyst coincides with one of the electrical axes of quartz; the latter is different for the three colour sectors usually appearing in a crystal of amethystine quartz. The right or left-handedness of the crystal determines which of the two axes meeting a particular rhombohedral face is the symmetry axis of the amethyst in the colour-sector contiguous to that face. For vibrations along the monoclinic symmetry axis, the colour of the transmitted light is a light orange with a maximum of absorption in the spectrum near 5000 Å. For vibrations along the two other colour axes, the colour of the transmitted light is respectively blue with an absorption maximum near 5750 Å and a deep reddish-purple with an absorption maximum near 5250 Å. These two axes lie in a plane perpendicular to the symmetry axis and make angles of approximately 45° on either side with the *c*-axis of quartz. The latter coincides approximately with the acute bisectrix in the biaxial figure.

In the present paper, we shall report some further experimental results and proceed to make some suggestions regarding the structure of amethyst which offer a pathway to the explanation of its optical behaviour. Some

evidence is also presented which throws light on the very interesting question of the genesis of amethyst in nature.

## 2. AMETHYST AND SMOKY QUARTZ

With our earlier paper, photographs were reproduced to illustrate the very significant difference between amethyst and smoky quartz in their optical behaviour, *viz.*, that the former does not exhibit the diffusion so conspicuously evident in the case of the latter when traversed by a pencil of light. We have since obtained somewhat better pictures exhibiting this difference, which are reproduced as Figs. 1, 2, 3 and 4 in Plate XVII accompanying the present paper. For recording these photographs, the specimen under study was immersed in a flat-sided cell containing freshly distilled benzyl alcohol which has a refractive index nearly the same as that of quartz. A narrow beam of sunlight traversed the specimen thus immersed and the cell was viewed transversely and photographed with approximately the same exposure time in each case.

Figure 1 is a record obtained with a polished cylinder of optically clear Brazilian quartz. Visually, a faint blue track could be seen, but a much longer exposure time than that actually employed would have been necessary to record the same. The track of the beam in the benzyl alcohol however appears with great intensity.

Figure 2 is a similar record obtained with a polished sphere of smoky quartz which had been specially prepared from a rounded pebble from Ceylon presented to us by Dr. C. S. Pichamuthu to whom our thanks are due. The specimen was only faintly smoky, but nevertheless, as can be seen from Fig. 2, the track of the beam was conspicuously visible, and was many times brighter than the track in colourless quartz as seen visually. The progressive extinction of the incident beam in traversing the smoky quartz is very evident in Fig. 2. The scattered light is, of course, also enfeebled by absorption before its emergence.

Figures 3 and 4 are slightly enlarged reproductions of photographs obtained with two strongly coloured amethyst gem-stones in our possession. In neither case does the interior of the crystal exhibit any visible evidence of the passage of the light through it. The track of the beam in the benzyl alcohol is weaker after its passage through the amethyst than before it. This is to be expected in view of the absorption of light in the crystal which is strongest in the green, yellow and orange regions of the spectrum. A similar absorption would necessarily also operate on the scattered light, if any, before

it emerges in a transverse direction. But since the shorter wave-lengths in the visible spectrum are the least absorbed in amethyst and would also be the strongest in the light scattered by it and since also, the thickness needing to be traversed is relatively small owing to the particular shape of our specimens, such absorption would in no way have prevented the observation of a Tyndall effect, had this been actually present.

### 3. THE DIAMAGNETIC BEHAVIOUR OF AMETHYST

In view of a recent report which appeared in the columns of *Nature*<sup>3</sup> claiming that strongly coloured specimens of amethyst are paramagnetic and that the colour of amethyst is accordingly to be ascribed to the presence of ferric iron in it, we thought it worthwhile even before our first paper was published to make some qualitative tests to ascertain the true position regarding this matter. In view of the very high paramagnetism exhibited by oxides of iron, very small percentages of the same present as included material would suffice to give wholly misleading results regarding the magnetic behaviour of amethyst. It is accordingly of the highest importance to use selected specimens shown by rigorous optical test to be free from such inclusions. In our preliminary observations, we used the same cut and polished gemstones as those for which the densities had been determined and reported

TABLE I  
*Comparison of Diamagnetic Susceptibilities*

Description	Mass in grams	Density in gm. per c.c.	Deflection in the Magnetic field: Scale divisions
<i>Amethyst</i>			
Intensely coloured ..	2.3394	2.651	9.1
Do. ..	1.8521	2.652	9.2
Do. ..	1.3466	2.651	9.0
Do. ..	1.0846	2.652	9.0
Do. ..	0.7137	2.650	7.0
Moderately coloured ..	2.2276	2.651	9.3
Do. ..	1.4184	2.650	8.0
Do. ..	1.2545	2.650	9.0
Lightly coloured ..	1.1595	2.653	8.7
Do. ..	1.1937	2.651	8.8
Do. ..	1.0351	2.650	9.0
Do. ..	0.7481	2.654	9.0
<i>Colourless quartz</i> ..	0.7481	2.650	9.1
Do. ..	0.334	..	9.1

in our first paper. Each specimen was tested in turn by attaching it to the end of a long vertical fibre and placing it in a powerful non-homogeneous magnetic field. When the electromagnet producing the field was excited, the specimen moved to a different position at which the restoring force due to its weight was balanced by the force of magnetic repulsion. The displacement produced would, in these circumstances, be determined by the mass-susceptibility of the specimen and independent of its size. Tested in this way, all the specimens listed in our earlier paper were found to be diamagnetic, and there were no noticeable differences in their behaviour in this respect.

To place the matter beyond all doubt, we have repeated these preliminary studies with improved technique. Each of the specimens under study was hung by a single rayon fibre about a metre long enclosed in a glass tube to protect it from disturbing air currents. A permanent magnet fitted with wedge-shaped pole pieces was employed to produce a non-homogeneous field. The magnet itself could be moved in such a manner that the specimen originally hanging in field-free space was transferred to a pre-determined position in a suitably chosen part of the field. The resulting displacement of the specimen was read off from the movement of the suspending fibre seen optically projected on a distant scale. Table I gives the results of measurements made with our specimens of amethyst, as also with pieces of colourless quartz. The data leave no room for doubt that, *to a first approximation, amethyst and quartz have the same magnetic susceptibility*. It is thus clear that the results reported in *Nature* and referred to above were based on observations made with impure and therefore unsuitable material. Incidentally, it should be mentioned that the difference between the diamagnetic susceptibility of colourless quartz along directions parallel and perpendicular to the trigonal axis as reported in the same communication is some twenty to thirty times larger than the actual difference. The latter is quite small, being indeed a little less than one half of one per cent. of the susceptibility in either direction.

#### 4. CRYSTAL STRUCTURE OF AMETHYST

As is well known, quartz in its low and high temperature forms possesses structures which are very similar to each other, though differing in detail. In either case, the unit cell contains three  $\text{SiO}_2$  groups, the silicon atoms being disposed in planes perpendicular to the trigonal axis of symmetry which divide the cell length into three equal parts. The oxygen atoms in high quartz are situated in three planes half-way between those containing the silicons, while in low-quartz they appear in six planes which are nearly

but (according to a recent report) not quite those of aliquot subdivision of the *c*-axis into nine equal parts. While the silicon atoms are situated in the special or symmetric positions in high-quartz, they are displaced from those positions in low-quartz and located on the three digonal axes of symmetry of the structure. The *c*-axis in either case is a screw axis, six-fold and three-fold respectively in the two cases.

If in the low-temperature form of quartz we imagine *one* of the **three** silicon atoms in the cell to be displaced along the digonal axis on which it lies, either towards or away from the position it would occupy in high-quartz, all the symmetry elements of the low-quartz structure would disappear, **except** the digonal axis in question. The modified structure would then possess only monoclinic symmetry. The same would continue to be the case **if** the two other silicon atoms in the cell are also displaced along their respective digonal axes, the magnitude of such displacement being the same for **both** but differing either in sense or magnitude or both from that of the first silicon atom. Any movement of the silicon atoms would necessarily involve movements of the oxygen atoms linked to them, as also a deformation of the oxygen tetrahedra surrounding the silicons. It would be easy however to picture such displacements of the oxygen atoms as would preserve the monoclinic symmetry contemplated above.

Thus, by a relatively simple and not improbable alteration in the structure of low-quartz, we arrive at a modification thereof possessing only monoclinic symmetry, the diad axis characteristic of such symmetry coinciding with **one** of the electrical axes of quartz in the undisturbed state. This is the situation which actually exists in amethyst as is shown by the study of its birefringence and pleochroism. We are therefore justified in pursuing the hypothesis and developing its consequences further. Since the surviving diad axis of symmetry may be any one of the three electrical axes of low-quartz, it follows immediately that there are three possible species of amethyst which are however different only in respect of their orientation within the colourless quartz. We thus arrive at an immediate explanation of the fact that the amethystine colour in quartz usually appears in three sectors, the orientation of its monoclinic axis altering by  $120^\circ$  when we pass from one sector to the next.

Figures 1 and 2 in Plate XVIII accompanying the present paper illustrate the feature referred to. These photographs were obtained of two crystals of amethyst immersed in a cell of benzyl alcohol by the light of a sodium vapour lamp transmitted through it. Figure 1 shows only two colour sectors, the absence of a third sector being readily understood as the corresponding

rhombohedral face was absent in the external form of the crystal. In Fig. 2 the three colour sectors are seen but are of very different sizes, such difference also being manifest in the external development of the corresponding rhombohedral faces. Figures 3 and 4 in Plate XVIII illustrate another feature very commonly observed in amethystine quartz. They are photographs of cut gem-stones viewed by transmitted light under immersion. Figure 3 exhibits one set of internal lamellæ consisting of alternate layers of colourless quartz and of amethyst, while in Fig. 4, two such sets are seen. In each case, the lamellæ are parallel to the rhombohedral planes in the quartz structure.

#### 5. THE OPTICAL PROPERTIES OF AMETHYST

The change from trigonal to monoclinic symmetry would necessarily involve an alteration in the optical behaviour of amethyst as compared with that of colourless quartz. The low birefringence of quartz is explicable as arising from the approximately tetrahedral grouping of the oxygen atoms around each silicon atom, while its optical activity is a consequence of the presence of a screw axis in the structure. Since amethyst possesses only monoclinic symmetry, it should be optically biaxial, the symmetry axis being one of the optic vibration directions; the other two would lie in a plane perpendicular to it. The trigonal axis is the direction of maximum polarisability in quartz, and if the changes of polarisability produced by the change of structure are small, the same direction would continue to be the direction of maximum polarisability also in amethyst. The *c*-axis of quartz would then appear as the acute bisectrix in the biaxial figure exhibited by amethyst between crossed polaroids. It may be presumed that there would also be noticeable changes in optical activity, but these would probably not be large.

Colourless quartz is quite transparent in the visible and ultraviolet regions of the spectrum but exhibits complete opacity even in thin layers beyond 1436 A.U. Chandrasekhar<sup>4</sup> has shown that the optical rotatory dispersion of quartz is represented accurately by a single-term formula containing a characteristic wave-length at 926 A.U. and that the refractive dispersion is also tolerably well represented by a single-term formula of the Drude-Sellmier type containing the same wave-length, both in respect of the ordinary and extraordinary indices with only a change in the oscillator strength as between these two. It would seem therefore that the absorptions present at wave-lengths greater than 926 A.U. influence the refraction and dispersion only to a minor extent. The high transparency of quartz in the visible and ultraviolet is undoubtedly a consequence of the saturated

character of the silicon-oxygen bonds and their tetrahedral grouping in the crystal. As already remarked, the change in structure from quartz to amethyst would necessarily involve a distortion of the oxygen tetrahedra surrounding each silicon. It is not unreasonable to assume that it is this distortion which is responsible for the appearance of the absorption bands in the visible and near ultraviolet characteristic of amethyst. In view of its monoclinic symmetry, the diad axis is necessarily one of the axes of the absorption ellipsoid, the other two lying in a plane perpendicular to it. Since the edges of the oxygen tetrahedra are variously inclined to the *c*-axis of quartz, there is no reason to assume that the latter would itself be one of the colour axes, and indeed actually it is not.

#### 6. THE GENESIS OF AMETHYST

A great collection of amethystine quartz collected by one of us some years ago from the University area near Hyderabad City in South India was available to us for examination. Certain general features observed with this material will now be described, as they are very illuminating in relation to the problem of the genesis of amethyst in nature.

An exceedingly common feature in our specimens is the appearance of an intense amethystine colour in the lower part of the crystal, the same being sharply terminated by one or more rhombohedral planes, while the upper part of the crystal is either completely colourless or exhibits a very light colour arranged in layers parallel to the same rhombohedral faces. A convenient way of exhibiting this feature is to immerse the crystal in a flat-sided cell containing benzyl alcohol and to photograph the same by the transmitted light of a sodium vapour lamp. The coloured regions appear quite dark in the resulting photograph, while the outer regions are almost completely transparent except for faint shadows due to defects in the material or the light colouration existing therein. Figures 3, 5 and 6 in Plate XX represent typical examples of this kind, the two former pictures representing the same crystal as viewed in perpendicular directions transverse to the *c*-axis.

A different and very illuminating procedure is to obtain a radiogram of the entire crystal or of a suitable section of it. Figures 1 and 2 in Plate XIX represent optical photographs of two such sections which were each about 5 mm. thick parallel to the *c*-axis, while Figs. 3 and 4 are radiograms respectively of the same specimens taken with the X-ray film quite close to the crystal. In the two former pictures, the transparent and coloured regions of quartz exhibit an intense contrast. *No such contrast appears in the radiogram, and indeed after many trials we have been unable to observe*

*the smallest difference between the X-ray transmissions of colourless and amethystine quartz.* A very interesting feature is however noticeable in Figs. 3 and 4. This is the appearance of a dome or a layer, as the case may be, of material quite opaque to X-rays. This layer is viewed edgewise in the radiogram in Fig. 4 and hence appears as a single dark streak, while in Fig. 3 it is viewed sideways and appears resolved into a large number of small specks lying on the boundary between the coloured and uncoloured quartz and forming a pyramidal dome having the same shape as that boundary. This material can easily be taken out and subjected to chemical analysis and discloses itself to be ferric oxide.

The same phenomenon as seen in a thick transverse section is represented in Figs. 1 and 4 of Plate XX, the former being the optical photograph and the latter an X-radiogram. The pattern of sectors of coloured and colourless quartz which is so conspicuous in the central region of Fig. 1 is completely absent in Fig. 4, but the encompassing hexagonal ring of particles of ferric oxide shows up clearly in both the pictures. Figure 2 in Plate XX is an optical photograph of a thin transverse section cut through a part of another crystal so chosen that the dome of ferric oxide is seen in its entirety. The dark area at the centre is in fact a dense aggregate of particles of that material. To the left of it is seen a thin layer of coloured amethyst stretching out from one of the edges of the same area.

The features described and illustrated above are equally well exhibited by thousands of other specimens in our collection. The inference suggested thereby seems irresistible, namely that the transformation from colourless quartz to amethyst occurs during the growth of the crystal and that the change of structure from trigonal to monoclinic symmetry is brought about by the presence of the ferric impurities in the crystallising material and during their progressive expulsion from the growing crystal. At some stage during this process, the ferric oxide separates completely, forming aggregates and thereafter ceases to play any role, the further crystallisation appearing in the form of colourless quartz. This hypothesis completely accounts for the very close relationship between the form and extension of the colour sectors of the amethyst and the form of the encompassing dome of ferric oxide particles, as also of their very obvious relationship to the external form of the crystal.

## 7. SUMMARY

Amethyst is diamagnetic, its susceptibility being not measurably different from that of colourless quartz. The optical characters indicate only monoclinic symmetry, of which the diad axis coincides with one of the three electric



FIG. 1

FIG. 2

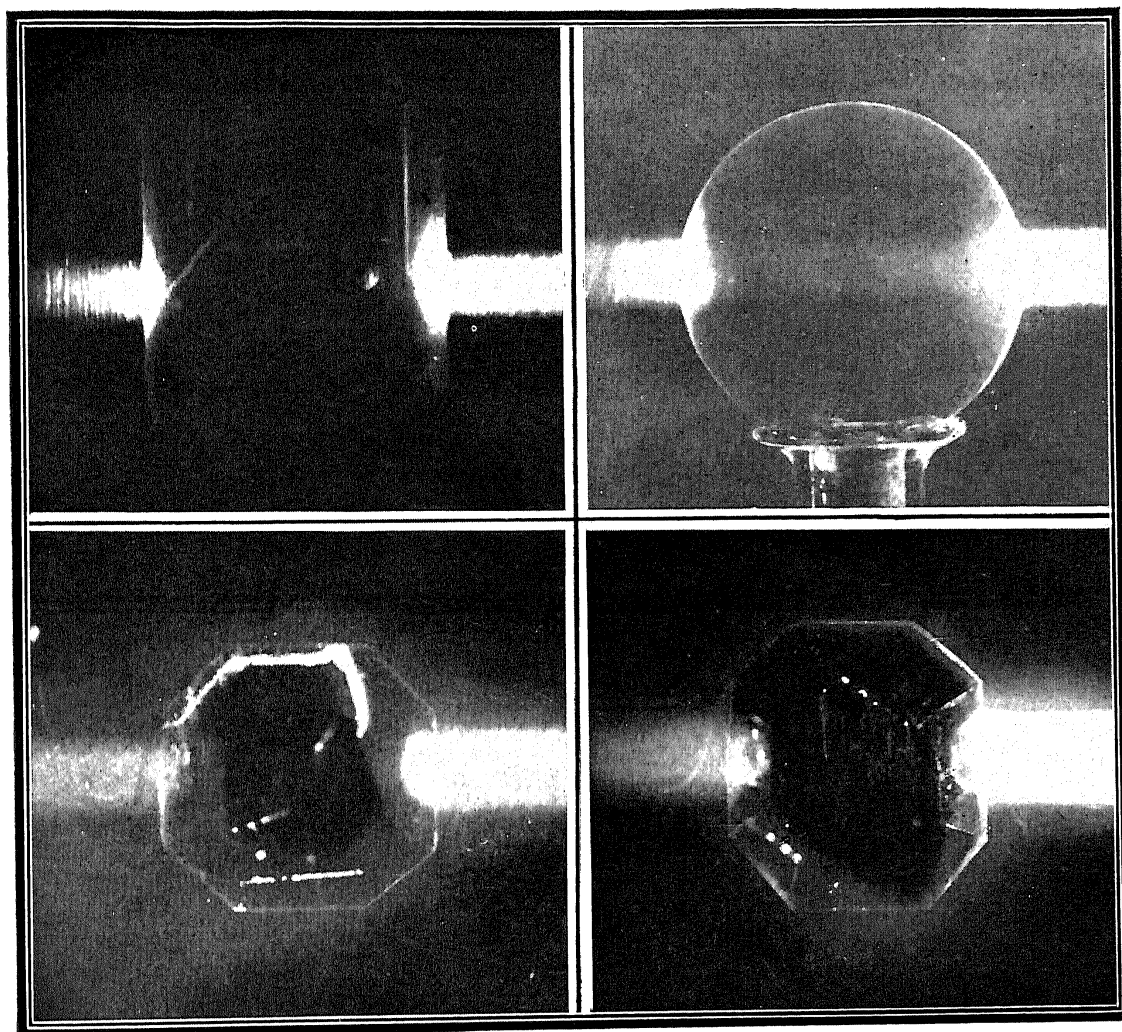


FIG. 3

FIG. 4

Scattering of Light in Smoky Quartz and Amethyst

FIG. 1

FIG. 2

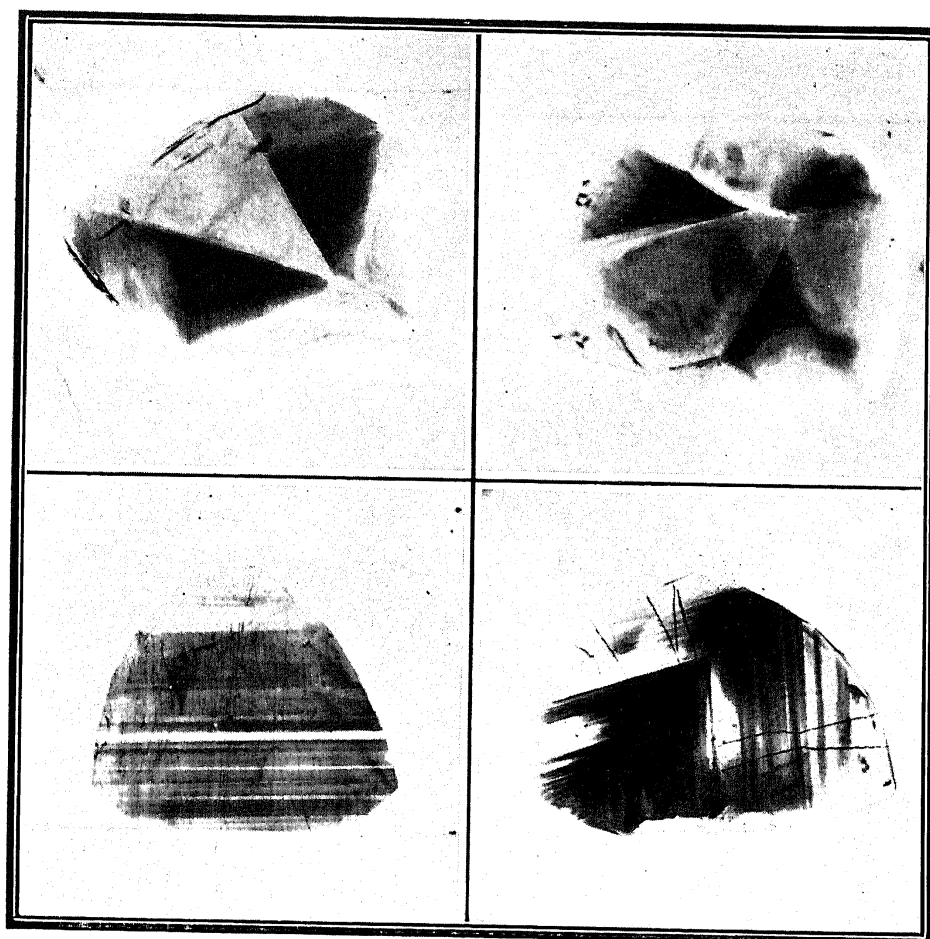


FIG. 3

FIG. 4

Colour-Sectors and Colour-Layers in Amethyst

FIG. 1

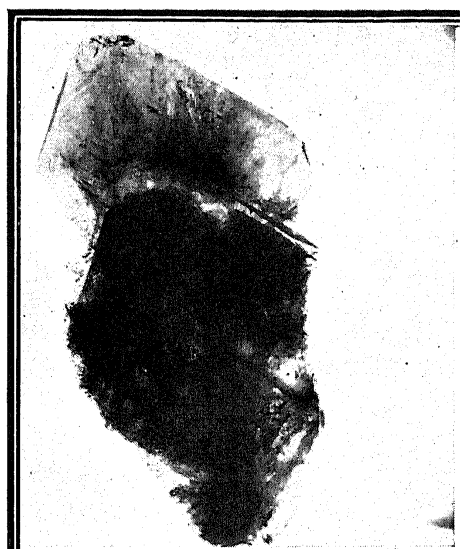


FIG. 3

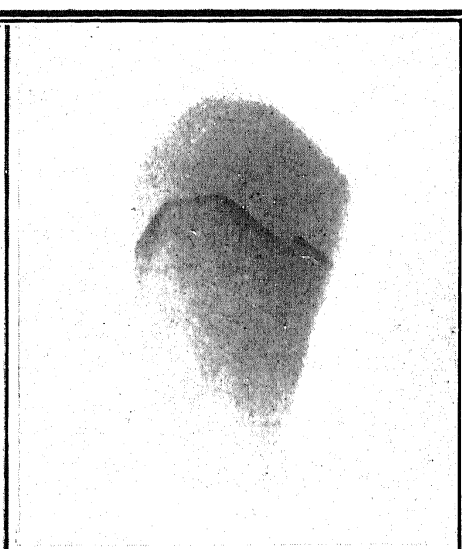


FIG. 2

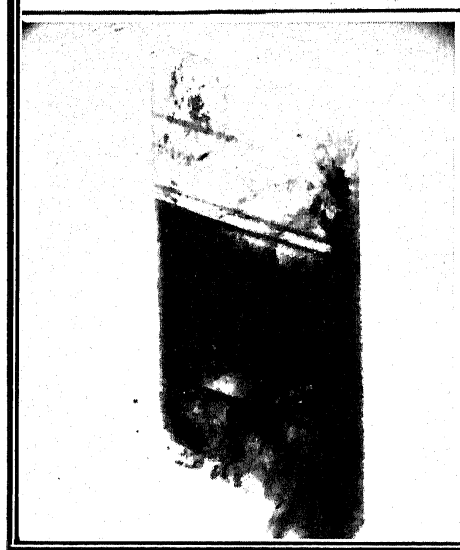
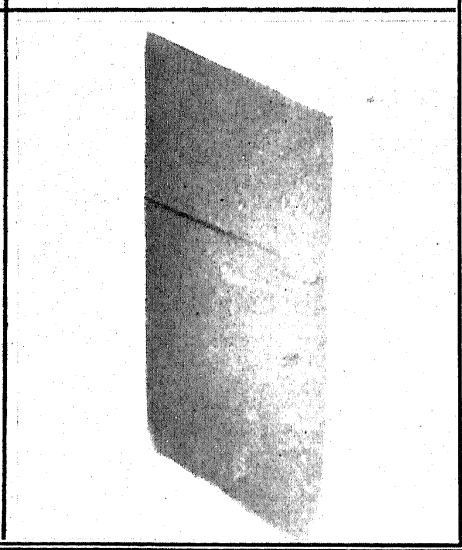


FIG. 4



Photographs and Radiograms of Amethyst

FIG. 1

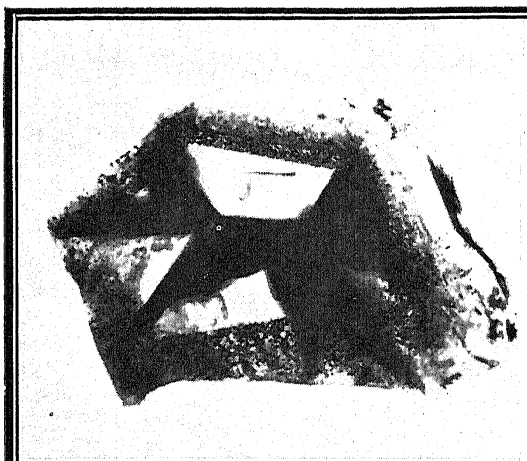


FIG. 4

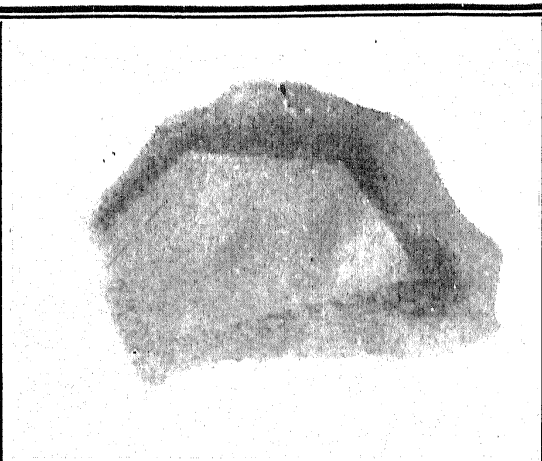


FIG. 2

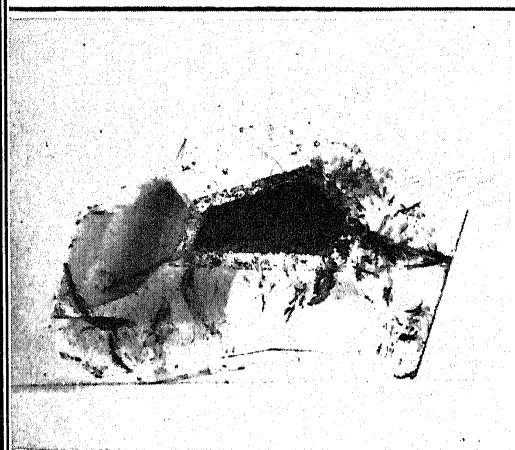


FIG. 5

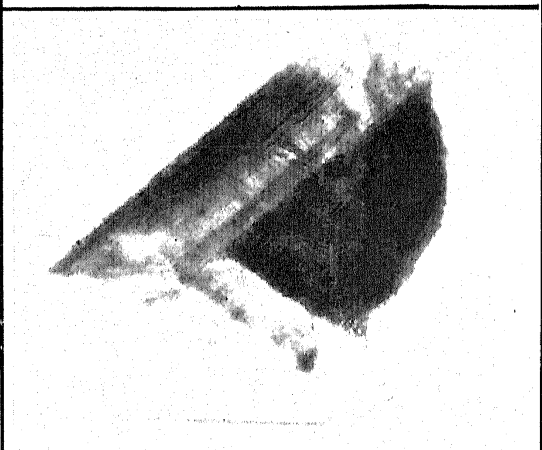


FIG. 3

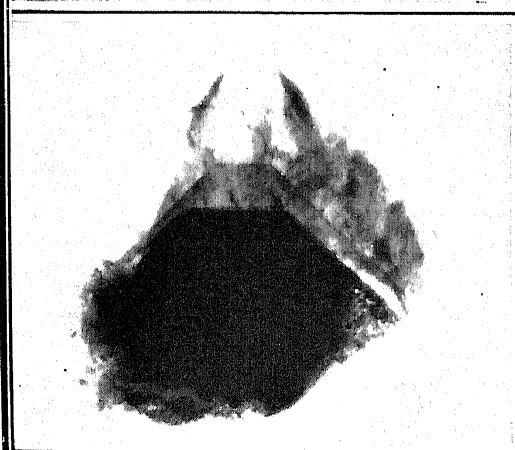
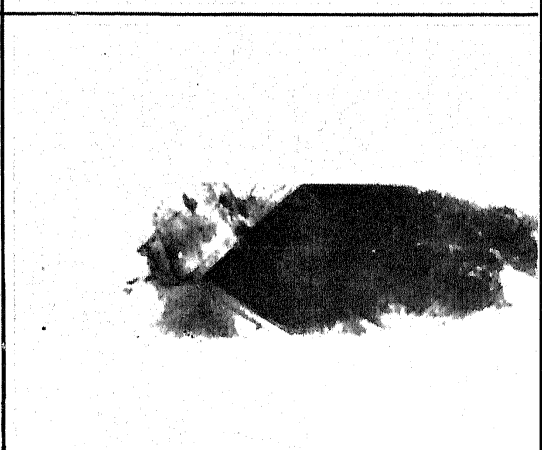


FIG. 6



Photographs and Radiogram of Amethyst

axes of the associated quartz. An immediate explanation of why three colour sectors usually appear in amethystine quartz is thus forthcoming. The nature of the modifications in structure which alter trigonal to monoclinic symmetry is indicated. A study of an extensive collection of material indicates that the change of structure occurs during the growth of the crystal from material containing ferric impurities and is consequential on the progressive elimination of these impurities which are finally deposited as a dome of discrete particles on the boundary between the amethyst and the colourless quartz.

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