

values mentioned heretofore in the literature are too high.

It would be a useful task to measure by this method the thicknesses of thin interference surface films by using maxima not only of the first order, but mainly those of higher orders. Films on glass offer only limited possibilities in this respect since they give only maxima of the first and partially of the second order. More suitable for this study would be monomolecular films as produced and studied by K. B. Blodgett, for it is possible to lay these monomolecular layers on each other to any thickness.

In conclusion some practical consequences

following from the study of physical properties, such as refractive index and thickness, of films on lead glass may be mentioned. By an optical method this superficial film was identified as a film of quartz glass. This thin, but very hard film of quartz glass can give good protection against mechanical damage to the soft lead glass (for example, of lenses). Another question is, whether the vessels of various types of lead glass, for example dishes, can be dangerous to life or not owing to chemical reaction with an acid. Finally, thin surface films on glass may be used in practice for producing glass articles showing iridescent colors.

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A Direct Comparison on a Crystal of Calcite of the X-Ray and Optical Interferometer Methods of Determining Linear Thermal Expansion

Evidence of Differences Among Calcite Crystals*

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Measurements by the x-ray and optical interferometer methods on the same specimen of calcite gave values for the coefficient of linear expansion which agree within the limit of measurement. Comparison of these results with data for other crystals of calcite shows that there is a significant difference in the expansion of different crystals. The spacing between the (211) [(100)] planes is also measurably different.

IN a recent determination of the thermal dilatation of calcite, Weigle and Saïni,¹ using an x-ray powder method, obtained coefficients for the expansion along the two principal crystallographic axes which were approximately 20 percent lower than those obtained by Benoit,² whose data, obtained by means of an optical interferometer, have hitherto been regarded as among the best available. This discrepancy, which is many times greater than the combined experimental error, indicates either that the two

methods do not give comparable results or that there is a significant difference in the expansion of different crystals of calcite. As measurements of the dilatation of sodium nitrate by the same x-ray method³ had given values in satisfactory agreement with data obtained by means of the interferometer,⁴ it seemed likely that the discrepancy with calcite was due to a difference in the specimens tested, a view which is supported by the difference in density among calcite crystals observed by DeFoe and Compton.⁵

* A preliminary note describing these results has been given by Saïni, *Compte rendu des Séances, Société de physique et d'histoire naturelle de Genève* **52**, 108 (1935).

¹ J. Weigle and H. Saïni, *Helv. Phys. Acta* **7**, 257 (1934).

² J. R. Benoit, *Trav. Bur. Int. Poids et Mesures* **6**, 190 (1888).

³ H. Saïni and A. Mercier, *Helv. Phys. Acta* **7**, 267 (1934).

⁴ J. B. Austin and R. H. H. Pierce, Jr., *J. Am. Chem. Soc.* **55**, 661 (1933).

⁵ O. K. DeFoe and A. H. Compton, *Phys. Rev.* **25**, 618 (1925).

If such a difference exists it is important that it be established beyond doubt and that its magnitude be determined, since calcite is commonly used as a standard grating in x-ray spectroscopy and the change in lattice spacing with temperature must be accurately known. For example, the coefficient of linear thermal expansion perpendicular to the (211) planes should be known to better than 1 percent if full advantage is to be taken of the precision of present x-ray technique.⁶

In order to determine to what extent the discrepancy between the data of Benoit and those of Weigle and Saïni is caused by the use of different experimental methods, measurements have been made by both x-ray and interferometer methods on the *same* crystal of calcite. The specimen selected, a large clear crystal from Big Timber, Montana, contained the following known impurities:

MgO less than 0.03 percent
MnO less than 0.06 percent
Fe less than 0.01 percent.

Small pieces were carefully cut from this block so that the linear expansion in four different directions within the crystal could be determined in an

TABLE I. Mean coefficients of linear thermal expansion between 18° and t°C. ($\alpha \times 10^6$.) The accuracy of coefficients determined optically is $\pm 0.5 \times 10^{-6}$, determined by x-rays it is 1.5×10^{-6} .

t°C	PARALLEL TO a AXIS PERPENDICULAR TO (112)		PERPENDICULAR TO ((011)) INTERFEROMETER	PERPENDICULAR TO RHOMBOHEDRAL FACE ((100)) (211) INTERFEROMETER	PARALLEL TO c AXIS PERPENDICULAR TO (111)	
	INTERFEROMETER	X-RAYS			INTERFEROMETER	X-RAYS
50	-4.9		0.1	10.8	25.1	
100	-4.8	-3.4	0.2	11.1	25.9	26.8
150	-4.8		0.4	11.4	26.8	
200	-4.8		0.6	11.6	27.4	
250	-4.8		0.8	11.8	27.8	
300	-4.7		0.9	12.0	28.1	

interferometer which has been described.⁴ The small pieces used in these determinations were then ground into powder and the expansion determined by the x-ray method used in the earlier measurements on calcite.¹

The results of the two sets of measurements, shown in Table I and Fig. 1, agree within the limit of accuracy of measurement, thus demon-

⁶ Cf. C. D. Cooksey and D. Cooksey, *Phys. Rev.* **36**, 85 (1930).

strating that the methods are comparable and should, in general, give the same values for the several coefficients. Since the x-ray method gives directly the expansion along the *a* and *c* axes, and does not give directly the expansion along the other directions studied with the interferometer, only the two coefficients for the axes are included in Table I. Coefficients for other directions as calculated from the x-ray data are given in Fig. 1, in which the several coefficients are plotted as a function of the square of the cosine of the angle between the *c* axis and the direction in which the expansion was determined, a method of plotting which gives a straight line for rhombohedral crystals. Planes perpendicular to the direction in which the expansion was measured are indicated by Miller indices with parentheses used according to the convention of Ewald and Hermann.⁷ It will be observed that although the difference between the two sets of measurements always lies within the experimental error, the coefficients determined by the x-ray method are consistently the higher, which may indicate a significant difference between the methods, but if so, the difference is small and can be established only by more accurate determinations. In any case, a possible difference of this sort is very much

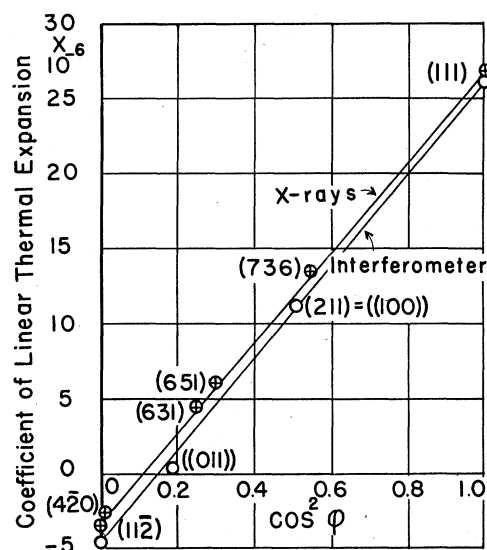


FIG. 1. Thermal expansion coefficients for different directions in a crystal of calcite as determined by x-ray and optical interferometer measurements on the same sample.

⁷ P. P. Ewald and C. Hermann, *Strukturbericht*, 1913-26 (Akademisches Verlagsgesellschaft, Leipzig, 1931), p. 293.

TABLE II. *Thermal expansion coefficients of calcite as reported in the literature*

INVESTIGATOR	TEMP. RANGE °C	LINEAR EXPANSION COEFFICIENT $\times 10^6$	
		PERPENDICULAR TO (111)	PERPENDICULAR TO (112)
Mitscherlich ¹	Room Temp. to 100°	28.6	-5.6
Fizeau ²	0 to 100°	26.4	-5.3
Pfaff ³	0 to 100°	26.3	-3.1
Benoit ⁴	18° to 100°	25.7	-5.5
Kozu, Masuda and Ueda ⁵	20° to 100°	22.5	-6
Kozu, Masuda and Ueda ⁵	20° to 100°	21.2	-6
Weigle and Saini ⁶	18° to 100°	21.0	-3.8
Austin and Pierce ⁷	20° to 100°	28.0	-5.0
Adenstedt ⁸	-20° to 0°	24.6	-5.6
This research—x-ray Interferometer	18° to 100°	26.8	-3.4
	18° to 100°	25.9	-4.8

¹ E. Mitscherlich, cf. C. Hintze, *Handbuch der Mineralogie* (Walter de Gruyter & Co., Berlin, 1930), Vol. 1, Part 3, p. 2859.² H. Fizeau, cf. C. Hintze, *Handbuch*, reference 1.³ F. Pfaff, *Pogg. Ann.* **104**, 171 (1858); **107**, 148 (1859).⁴ J. R. Benoit, *Trav. Bur. Int. Poids et Mesures* **6**, 190 (1888).⁵ Kozu, Masuda and Ueda, *Sci. Reports, Tohoku Imp. Univ.* [III] **3**, 247 (1929).⁶ J. Weigle and H. Saini, *Helv. Phys. Acta* **7**, 257 (1934).⁷ J. B. Austin and R. H. H. Pierce, Jr., unpublished data for a sample used for analytical standardizations.⁸ H. Adenstedt, *Ann. d. Physik* [5] **26**, 69 (1936).

smaller than the observed differences among samples. For example, the coefficients for the sample from Big Timber are in fair agreement with those reported by Benoit² but differ by over 20 percent from those for the sample previously studied by Weigle and Saini, a difference which can only be accounted for as a difference between the samples.

As further evidence for the existence of differences among samples, we have collected the several sets of data reported in the literature and have in Table II compared them with our results and with another set of hitherto unpublished measurements obtained by means of the interferometer. The coefficient for the direction perpendicular to the *a* axis is small, in fact, its magnitude is only two or three times the experimental error in some cases, hence, a relatively large variation is to be expected, but the expansion along the *a* axis is so large that the observed variation of nearly 30 percent among the values for this coefficient cannot be ascribed to any error of measurement. It should be noted in particular that there are significant differences among the coefficients obtained with different samples by the same investigators using the same method. Thus, Weigle and Saini obtained $21.0 \pm 1.5 \times 10^{-6}$ for their first sample as compared with $26.8 \pm 1.5 \times 10^{-6}$ for the sample from Big Timber and Austin and Pierce obtained $28.0 \pm 0.5 \times 10^{-6}$ for a sample used as an analytical

standard as compared with $25.9 \pm 0.5 \times 10^{-6}$ for the sample from Big Timber.

The coefficient for the direction perpendicular to the (211) [or ((100))] planes, derived from the several sets of data for the expansion along the *a* and *c* axes by means of a cosine plot similar to Fig. 1, varies from 7.8×10^{-6} to 12.0×10^{-6} , a variation much greater than is permissible in x-ray measurements of the highest precision. These are, of course, mean coefficients for the range 18° to 100°C and it is not impossible that the coefficient for a smaller range, say 18° to 25°C, would show a smaller variation, yet even so, the variation is certain to be larger than 1 percent which is the desired accuracy.

It is also of interest to compare the distance between the (211) [or ((100))] planes at 18°C for different samples. The value for the sample studied previously by Weigle and Saini is 3.0262×10^{-8} cm, whereas that determined on the present sample is 3.0290×10^{-8} cm. The value recommended by Siegbahn is 3.02904×10^{-8} cm for small Bragg angles and 3.02945 for a limiting angle of 90°. As the present measurements were made with a Bragg angle of 75°, the value for the sample from Big Timber differs by 1 part in 10,000 from the Siegbahn value whereas the parameter of the Weigle and Saini sample shows a difference of 1 part of 1000. There appears, therefore, to be a difference in grating space as well as in the coefficient of linear expansion.