



# Vacuum Ultraviolet Photochemistry. Part III. Acetylene at 1849 A

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## Vacuum Ultraviolet Photochemistry. Part III. Acetylene at 1849 A

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The products of acetylene photolysis at 1849 A were found to be a polymer resembling cuprene, hydrogen, ethylene, diacetylene, vinylacetylene, and benzene. The relationships of the quantum yields of these products to pressure of acetylene suggest that both free radicals and excited acetylene molecules are involved in the photolytic mechanism. This suggestion is strongly supported by the nature of the absorption spectrum, since in this wavelength region, the absorption is partly discrete and partly continuous.

#### I. INTRODUCTION

HE photochemistry of acetylene has been the subject of numerous investigations.<sup>1-7</sup> All workers seem to agree that the chief effect of light absorption or of collision with Hg  $({}^{3}P_{1})$  is polymerization, most likely involving excited acetylene molecules. In more recent work,<sup>8</sup> LeRoy and Steacie suggest that the mercury sensitized polymerization of acetylene proceeds at least partially by a free radical mechanism. They propose that none of the previous work on acetylene is inconsistent with a free radical process, although they admit that all results can also be explained by an excited molecule mechanism. The present work was undertaken as an attempt to reach a conclusion favoring either one or both explanations.

#### **II. EXPERIMENTAL**

The acetylene used for these measurements was prepared from tank gas by bulb to bulb distillation, using liquid nitrogen as the refrigerant. The purity of the final product was checked on the Consolidated Engineering Corporation Analytical Mass Spectrometer, and found to contain no detectable impurity. Since the mass spectrometer had been modified to improve its usual sensitivity,\* the upper limit of impurity must be placed as one part in 10 000. This improved sensitivity made it possible to study acetylene photolysis at a very low extent of reaction (<5%). This procedure has obvious advantages since many of the products formed (benzene,

vinylacetylene, etc.) would begin to absorb an appreciable portion of the incident light were their concentrations allowed to become sizeable. Such a circumstance would lend much confusion to the interpretation of results, particularly at 1849 A where the absorption of benzene is very strong.9 Further benefit is gained through the prevention of extensive solid polymer formation at these low degrees of reaction. All workers on acetylene are well aware of this deposition of solid material on the walls of the reaction vessel and the resulting opacity of the vessel to the incident ultraviolet light.

The lamp used for this work was a low pressure quartz mercury arc<sup>10</sup> having a very high output at 1849 A. Since acetylene is practically transparent to 2537 A<sup>4</sup> and has an absorption coefficient of 20 cm<sup>-1</sup> at 1849 A,<sup>11</sup> it is evident that 1849 A was the "active" radiation in these experiments. The exposure time was usually of the order of three minutes, after which the lamp was shut off and the gaseous products analyzed on the mass spectrometer. Even though the exposures were short, the lamp received an opaque polymeric deposit which reduced the light output considerably so that cleaning with nitric acid was necessary at frequent intervals. This deposit made absolute quantum yield measurements fairly uncertain, although a good deal of information can be had from reliable relative quantum yields which were easily obtainable. To deal experimentally with this situation, it was necessary to make intensity calibration runs immediately before and immediately after an acetylene run. These calibrations used nitrous oxide photolysis, the quantum yield of which is known fairly well.<sup>10</sup> The times for acetylene exposures were chosen so that the intensity decrease seldom exceeded 25%. Repeated checks were made which showed that the intensity decreased in an approximately linear fashion at least up to 50% decrease. Thus a linear average of the intensity before and after C2H2 exposure probably involves an error no greater than 10%. Nevertheless, in

<sup>&</sup>lt;sup>1</sup> A. Thenard, Compt. rend. 78, 219 (1874).

<sup>&</sup>lt;sup>2</sup> D. Berthelot and H. Gaudechon, Compt. rend. **150**, 1169 (1910). <sup>3</sup> J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. **49**, 2438

<sup>(1927).
&</sup>lt;sup>4</sup> S. C. Lind and R. Livingston, J. Am. Chem. Soc. 54, 94 (1932).
<sup>6</sup> W. Kemula and S. Mrazek, Z. physik. Chem. B23, 358 (1933).
<sup>6</sup> S. C. Lind and C. H. Schiflett, J. Chem. Phys. 38, 377 (1934).

 <sup>&</sup>lt;sup>7</sup> H. W. Melville, Trans. Faraday Soc. 32, 258 (1936).
 <sup>8</sup> D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. 12, 117 (1944)

<sup>\*</sup> This modification was made by substituting a vibrating-reed electrometer (Model 30, Applied Physics Corporation, Pasadena, California) for the dc amplifier provided with the CEC Model 21-103 Mass Spectrometer. This substitution provides a manual switching arrangement which can be used at any ion peak during an analysis to increase that peak height by a factor of ten. The very low noise level, even with the increased sensitivity, made it possible to analyze gas mixtures containing very small amounts of contaminants (> 0.01%). We are indebted to Dr. R. F. K. Herzog of this laboratory who performed this modification.

W. C. Price and W. T. Tutte, Proc. Roy. Soc. (London) A174,

<sup>207 (1940).</sup> <sup>10</sup> M. Zelikoff and L. M. Aschenbrand, J. Chem. Phys. 22, 1685

<sup>&</sup>lt;sup>11</sup> This absorption coefficient is part of a set of data, as yet unpublished, which will be reported in the near future by K. Watanabe.

measuring quantum yields, since the degree of reaction was kept very low, the decrease of acetylene pressure was very small and could not be reliably measured. Since this pressure decrease is essential to the determination of the amount of C<sub>2</sub>H<sub>2</sub> disappearing, any single quantum yield reported must be looked at with suspicion. Nevertheless, it was observed that there was a definite increase in the quantum yield of C<sub>2</sub>H<sub>2</sub> disappearance with increasing C<sub>2</sub>H<sub>2</sub> pressure. Although the magnitude of this increase cannot be stated, the trend was quite clear, going from about 2 at the lower pressures (about 2 mm) to over 10 at higher pressures (ca 70 mm). The temperature in the reaction vessel was about 50°C. The quantum yields of formation of products are more reliable since they involve primarily the final acetylene pressure rather than the small pressure decrease. However, since the amounts of products were very small, a reasonable error must be assumed in their measurement. Taking into consideration the uncertainty in light intensity, the quantum yields of appearance of products can be accepted as more reliable than that for  $C_2H_2$ ; certainly their values, probably accurate within less than 25%, can be counted on to reveal a trend such as pressure effect.

## III. DATA AND DISCUSSION

The gaseous products formed from the  $C_2H_2$  photolysis at 1849 A were, as stated above, analyzed on a Consolidated Mass Spectrometer. Most of those found, i.e., vinylacetylene, benzene, ethylene, hydrogen, have been reported in the literature.<sup>1-8</sup> In addition, the present work has uncovered the presence of relatively large amounts of diacetylene. The data of Table I contain the quantum yields of formation of the products as a function of acetylene pressure. The hydrogen measurements are probably the least accurate and can only be relied on to show a slight trend. This lack of accuracy is not surprising for hydrogen in view of its low concentration and low sensitivity in mass spectrometric analysis. Indeed, in most of the experiments no analysis for hydrogen was made. Although the amounts of vinylacetylene are very small, analysis is quite reliable, owing to its high sensitivity.

The salient features emerging from an examination of Table I are:

(1) The quantum yield of disappearance of acetylene is much larger than that for the appearance of products and seems to show an increasing trend as the C<sub>2</sub>H<sub>2</sub> pressure increases.

(2) The quantum yield for the appearance of benzene shows a pronounced increase with increasing pressure.

(3) The quantum yield for the appearance of vinylacetylene is approximately the same as  $\varphi$  benzene at low pressures and shows a slight increasing trend as the pressure increases. This rate of increase is much smaller than the corresponding change for benzene.

(4) The quantum yield of appearance of diacetylene

TABLE I. Quantum yields  $(\varphi)$  of formation of products of acetylene photolysis and approximate  $\varphi$  C<sub>2</sub>H<sub>2</sub>.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	mm pressure C2H2	φH <sub>2</sub>	φC₂H₄	φ di- acetylene	φ vinyl- acetylene	\$ benzene	φC2H2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.67	0.039	0.049	0.106	0.009	0.008	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.81		0.048	0.093	0.006	0.004	2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.04		0.043	0.067	0.013	0.020	2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.01	0.038	0.072	0.135	0.014	0.025	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.08	0.036	0.057	0.126	0.009	0.009	3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.21		0.038	0.093	0.008	0.012	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3.94		0.039	0.112	0.008	0.012	2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.01		0.043	0.091	0.014	0.035	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.31		0.034	0.144	0.011	0.031	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.68	0.020	0.033	0.116	0.013	0.033	4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.95	0.020	0.032	0.122	0.011	0.029	5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5.5		0.049	0.087	0.016	0.058	3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5.9		0.046	0.070	0.011	0.030	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6.0		0.062	0.078	0.017	0.064	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6.4		0.055	0.091	0.009	0.024	• • •
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.6		0.036	0.099	0.009	0.022	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8.6		0.041	0.087	0.011	0.043	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9.6		0.035	0.088	0.012	0.061	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	11.7	0.022	0.039	0.132	0.017	0.080	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14.4		0.027	0.085	0.012	0.091	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22.6	0.021	0.054	0.100	0.020	0.140	15
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	30.4		0.060	0.100	0.013	0.160	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	47.2		0.050	0.157	0.017	0.149	15
74.0 0.047 0.125 0.016 0.170	53.5	0.020	0.040	0.107	0.010	0.197	
	74.0	•••	0.047	0.125	0.016	0.170	•••

is much larger than those of benzene and vinylacetylene at lower pressures, but  $\varphi$  benzene increases at high pressure to a value greater than that of  $\varphi$  diacetylene which does not change with pressure.

(5) The quantum yield of appearance of hydrogen is difficult to measure and the values given are not to be taken as quantitative. However, a decrease with increasing pressure seems evident.

(6) The quantum yield for the appearance of ethylene is larger generally than that for hydrogen and does not seem to have any pressure dependence.

Before attempting to interpret these observations from the standpoint of mechanism, and in consideration of the work of other investigators, a great deal of light can be shed immediately on the initial step of the mechanism by discussing the nature of the absorption spectrum in the 1800-2000 A region. Kistiakowsky<sup>12</sup> reported that pure acetylene is transparent down to 2400 A and begins to absorb weakly  $\sim$ 2377 A. Here a number of faint bands set in extending to about 2250 A. A continuous background sets in about 2350 A and becomes quite strong below 2250 A making observations of bands difficult at lower wavelengths. Stark and Lipp<sup>13</sup> had previously observed absorption bands down to 1900 A and Kistiakowsky therefore suggested that his observed continuum might be due to impurities. This suggestion was later supported by Dieke's<sup>14</sup> observations on acetylene in the region around 1900 A.

In previous work in this laboratory on absorption

 <sup>&</sup>lt;sup>12</sup> G. B. Kistiakowsky, Phys. Rev. 37, 276 (1931).
 <sup>13</sup> J. Stark and P. Lipp, Z. physik. Chem. 86, 36 (1913).
 <sup>14</sup> See W. C. Price, Phys. Rev. 47, 444 (1935).

coefficients<sup>15,16</sup> in the far ultraviolet, a method was described which employs a vacuum monochromator and photoelectric light intensity measurements. This detection method measures intensity in such a manner that small changes in absorption are easily detectable. Accordingly, it is possible to detect weak bands superimposed on a continuum. The results of a study<sup>11</sup> on the absorption coefficients of the extremely pure acetylene used in this work show that the region between 1800 and 2000 A contains a system of weak, comparatively diffuse bands superimposed on a continuum. Since the extent of impurity in the acetylene does not exceed one part in 10<sup>4</sup>, there can be very little doubt of the existence of the continuum. At 1849 A the absorption of acetylene is partly due to a band and partly to the continuous region. Hence, at the outset of this discussion, it must be pointed out that the initial absorption by  $C_2H_2$  leads both to dissociation and to an excited molecule. This fact must unavoidably color any interpretation put on the photochemical data. Careful observation of the spectrum seems to indicate that the continuous portion of the absorption of 1849 A is stronger than the discrete portion.

Strong corroborative evidence of the foregoing discussion is the formation of diacetylene and the independence of its quantum yield on pressure of C<sub>2</sub>H<sub>2</sub>. Thus, we may adopt as the first part of our mechanism

(a)  $C_2H_2 + \lambda \nu$  (1849 A) $\rightarrow C_2H + H$ 

(b) 2  $C_2H \rightarrow C_4H_2$ .

The formation of diacetylene by

(c) 
$$C_2H+C_2H_2\rightarrow C_4H_2+H$$

must be considered unlikely, since  $\varphi C_4 H_2$  does not increase with increasing  $C_2H_2$  pressure. The possibility of

(d) 
$$C_2H+C_2H_2 \rightarrow C_4H_3$$

leading to polymerization<sup>8</sup> is seriously questionable, since this would tend to decrease  $\varphi C_4 H_2$  with increasing pressure.

It is easier to explain the formation of polymer by

- (e)  $C_2H_2 + \lambda \nu$  (1849 A) $\rightarrow C_2H_2^*$
- (f)  $C_2H_2^*+C_2H_2 \rightarrow C_4H_4^*$

etc., with chain-stopping steps of the type

(g) 
$$C_4H_4*+C_2H_2\rightarrow C_6H_6$$
.

This has been proposed by Melville.<sup>7</sup> Presumably, the excited dimer, trimer, etc. molecules have the alternative of continuing the polymerization or not. That the chains are long is quite evident from a comparison of  $\varphi C_2H_2$  with  $\varphi C_6H_6$ ,  $\varphi C_4H_4$ , and particularly with  $\varphi$  C<sub>4</sub>H<sub>2</sub>. Note at low pressures that  $\varphi$  C<sub>4</sub>H<sub>2</sub> is much larger than  $\varphi C_6H_6$  and  $\varphi C_4H_4$  but still much smaller than  $\varphi$  C<sub>2</sub>H<sub>2</sub>. Evidence in favor of (e), (f), and (g) is the

pressure effect on  $\varphi C_4H_4$  and  $\varphi C_6H_6$  as well as on  $\varphi C_2 H_2$ . Since  $\varphi C_6 H_6$  increases much more rapidly with pressure than does  $\varphi$  C<sub>4</sub>H<sub>4</sub>, it might be suggested that the chain-ending step is a deactivating collision of an excited molecule with the wall. If this were so, one might expect that the pressure would have more effect on the quantum yields of higher aggregates.

LeRoy and Steacie, <sup>8</sup> using  $Hg(^{3}P_{1})$  sensitization, have observed nitric oxide inhibition of the rate of acetylene photolysis and suggest that the polymerization process involves free radicals. They therefore suggest

- (h)  $Hg(^{3}P_{1})+C_{2}H_{2}\rightarrow C_{2}H+H+Hg(^{1}S_{0})$
- (d)  $C_2H+C_2H_2\rightarrow C_4H_3$  etc.
- (k)  $H+C_2H_2\rightarrow C_2H_3$  etc.

They further state that the chain length is independent of pressure. This is rather difficult to reconcile with (d) and (k) and is not in accord with the measurements of the present work. Furthermore, at least (d) is unlikely, since  $\varphi$  diacetylene has been shown to be independent of pressure. Indeed, although Burnham and Pease<sup>17</sup> have found that NO inhibits the thermal polymerization of  $C_2H_2$ , they state that this inhibition differs from those of C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>. LeRoy and Steacie admit the possibility of reaction of NO with excited C2H2 to form  $C_2H_2$  NO as a cause of the inhibition. If a free radical is involved, the route to polymerization narrows down to Eq. (k). If this is to be accepted, in view of the high values of  $\varphi$  C<sub>2</sub>H<sub>2</sub>,  $\varphi$  benzene, etc., it is surprising that  $H_2$  is found at all, and moreover, that  $\varphi$   $H_2$  is so large compared with the other quantum yields. On the other hand, it must be admitted that (k) occurs at least to some extent. H atoms react with  $C_2H_2^{18}$  and  $C_2H$ radicals apparently do not participate in the polymerization. Moreover, if the only course open to hydrogen atoms were recombination to  $H_2$ ,  $\varphi H_2$  should equal  $\varphi$  C<sub>4</sub>H<sub>2</sub>. That this is not so is evident from Table I; also, not all the H atoms are used up in the formation of ethylene or  $\varphi$  C<sub>4</sub>H<sub>2</sub> would equal the sum of  $\varphi$  C<sub>2</sub>H<sub>4</sub> plus  $\varphi$  H<sub>2</sub>. Thus, even admitting that (k) must occur to some extent, one cannot easily explain the formation of vinylacetylene and benzene without resorting to some degree of artificiality and postulating processes which are improbable from purely a collision frequency point of view.

One may indeed ask if the mechanism does not involve both free radicals and excited molecules. It is the chief contention of this paper that both modes of reaction are involved. Dieke14 has reported no evidence of predissociation in the wavelength region of these experiments, hence some of the absorption must inevitably lead to excited molecules. The formation of

 <sup>&</sup>lt;sup>15</sup> Watanabe, Inn, and Zelikoff, J. Chem. Phys. 21, 1026 (1953).
 <sup>16</sup> M. Zelikoff and K. Watanabe, J. Opt. Soc. Am. 43, 756 (1953).

<sup>&</sup>lt;sup>17</sup> H. D. Burnham and R. N. Pease, J. Am. Chem. Soc. 64, 1404 (1942).

<sup>&</sup>lt;sup>18</sup> D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. 12, 369 (1944).

benzene and vinylacetylene as well as the pressure dependence of their quantum yields supports the excited molecule mode of polymerization. The continuous absorption superimposed on the banded region as well as the formation of diacetylene and hydrogen indicate that some of the initial absorption leads to dissociation. That some of the polymerization occurs through vinyl radicals formed from (k) cannot be eliminated although a plausible mechanism can be developed without (k). The question of differences in C<sub>2</sub>H<sub>2</sub> behavior towards  $Hg(^{3}P_{1})$  and  $h\nu$  (1849 A) is probably not serious. Using  $Hg(^{3}P_{1})$ , benzene,<sup>5</sup> ethylene,<sup>5</sup> and hydrogen<sup>8</sup> have been found. Probably diacetylene was not reported because its presence was not suspected.

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## Thermal Expansion and Stability of Layer Structures in Ionic AB Compounds\*

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Thermal expansion in PbO, SnO, or LiOH, in which single layers of  $O^{2-}$  or Li<sup>+</sup> alternate with double layers of Pb<sup>2+</sup>, Sn<sup>2+</sup>, or (OH)<sup>--</sup>, respectively, is relatively small normal to the layers (c-axis). This "anomaly" is related to asymmetrical dilatation of the polarizable Pb2+, Sn2+ in the field of O2- anions, or, respectively, to elongation of (OH)- in the field of Li<sup>+</sup>: When the cation-anion distance increases with temperature, the resulting decrease in these deformations reduces the spacing between the layers of like polarizable ions and the effective thermal expansion. Structures of this type are not stable for AB compounds if the polarized ion is the anion, but are if it is the cation: As cation polarizability increases with polarization, asymmetric, one-sided coordination of polarizing anions occurs, the energy being further lowered by dispersion forces acting between dilated cations. On the contrary, anions tightened by cations approach the behavior of rigid ions in coordinating cations more symmetrically in three-, rather than two-dimensional networks.

## INTRODUCTION

HERMAL expansion in layer structures usually is quite anisotropic. In graphite<sup>1</sup> and boron nitride<sup>2</sup> at low temperatures even small contraction within the layers accompanies the large expansion perpendicular to them. In calcium hydroxide<sup>3</sup> and magnesium hydroxide,3 coefficients of expansion normal to the layers are 3 to 4 times larger than those parallel to them. This behavior is generally attributed to weak binding between layers.<sup>4</sup> Observations of the reverse behavior, namely, small perpendicular expansion, are reported in the following. They were made with compounds of the type AB in which similarly as in Ca(OH)<sub>2</sub>  $(type AB_2)$  single layers of A ions alternate with double layers of B ions. These are "sandwich"-type layer structures:  $\cdots (B_n A_m B_n) (B_n A_m B_n) \cdots$ , for example

or

$$\cdots [(HO)_n Ca_n (OH)_n] [(HO)_n Ca_n (OH)_n] \cdots,$$
$$\cdots (Pb_n O_{2n} Pb_n) (Pb_n O_{2n} Pb_n) \cdots.$$

#### EXPERIMENTAL RESULTS

Measurements were carried out between 100 and 1000°K by means of x-ray diffractometers provided with devices permitting cooling with liquid nitrogen or heating. The lattice constants a, b, c and their expansion coefficients  $\beta_a$ ,  $\beta_b$ , and  $\beta_c$  could not be measured with high precision, but the determination of changes in the ratios (X = c/a or c/b) as a function of temperature was satisfactory. Table I and Figs. 1 and 2, show results obtained with the two enantiotropic forms of plumbous oxide, PbO, and with stannous oxide, SnO, "isostructural" with tetragonal PbO. Lithium hydroxide, LiOH, and ferrous selenide, FeSe, anti-isostructural with tetragonal PbO, were also investigated. Hexagonal cadmium iodide, CdI2, included as a most familiar example of layer structure, exhibits a "normal," strong anisotropy of thermal expansion in favor of the c-axis, perpendicular to the  $(I_n Cd_n I_n)$  "sandwiches" (Table I): Between 25 and 325°C,  $\beta_c$  is approximately  $4 \times 10^{-5}$  as against  $\beta_a \approx 1 \times 10^{-5} (^{\circ}C)^{-1}$ , i.e., X = c/a increases by approximately 1% (Fig. 1). Tetragonal stannous oxide, in a range of 275°, shows an increase in c/a of about 0.5%, i.e., behaves, at least qualitatively, as expected. However, LiOH, FeSe, and the red, tetragonal, lowtemperature form of PbO exhibit, despite the similarity in structure to SnO, constancy of the c/a ratio, i.e., isotropic expansion within the limits of error (Table I and Fig. 1). This "anomaly" is surpassed by the yellow, orthorhombic, high-temperature modification of PbO: c/a is essentially constant over a range of 850°, while c/b decreases by as much as 2.5% (Fig. 1). In other words, strongest expansion occurs, not in the c, but in

<sup>\*</sup> Work performed for the U. S. Atomic Energy Commission. <sup>1</sup> Compare, e.g., B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) 57, 477 (1945).

<sup>&</sup>lt;sup>2</sup> R. S. Pease, Acta Cryst. **5**, 356–361 (1952). <sup>3</sup> Helen D. Megaw, Proc. Roy. Soc. (London) **142**, 198–214 (1933).

<sup>&</sup>lt;sup>4</sup> Compare, e.g., E. Grüneisen and E. Goens, Z. Physik 29, 141 (1924).