We consider the flat back reflection camera in Fig. 1 and find,

$$\cos \varphi_i = -\cos 2\theta_i = 2 \sin^2 \theta_i - 1 = s/[s^2 + (\tfrac{1}{2}n_i)^2]^{\frac{1}{2}} . \quad (1)$$

For two different lines we have

$$(h_i^2 + k_i^2 + l_i^2)\lambda_i^2 = (2a)^2 \sin^2 \theta_i \quad (i = 1, 2) \quad (2)$$

which together yield

$$R \equiv (n_1/n_2)^2 = \frac{[((h_1^2 + k_1^2 + l_1^2)\lambda_1^2/2a^2) - 1]^{-2} - 1}{[((h_2^2 + k_2^2 + l_2^2)\lambda_2^2/2a^2) - 1]^{-2} - 1} .$$

If we now let $m_i = (h_i^2 + k_i^2 + l_i^2)\lambda_i^2/2$ and $x = 1/a^2$ we obtain

$$x^3 + px^2 + qx + r = 0 , \quad (4)$$

where

$$p = -2\frac{(m_1 + m_2)}{m_1 m_2} \quad (5)$$

$$q = \frac{(m_1 + m_2)^2}{(m_1 m_2)^2} + \frac{2}{m_1 m_2} + \frac{m_2^2 - Rm_1^2}{m_1^2 m_2^2 (R-1)} \quad (6)$$

and

$$r = -2\left[\frac{(m_1 + m_2)}{(m_1 m_2)^2} + \frac{(m_2 - Rm_1)}{m_1^2 m_2^2 (R-1)}\right] . \quad (7)$$

This cubic equation can readily be solved for a.

We can now investigate the error in $x = 1/a^2$ introduced by an error in $R = (n_1/n_2)^2$.

$$\Delta x = \Delta R(\partial x/\partial R) \equiv \Delta R . Z' \quad (8)$$

$$\begin{aligned} Z' &= (\partial x/\partial q)\,(dq/dR) + (\partial x/dr)\,(dr/dR) \\ &= \frac{2(m_1 - m_2) - x(m_1^2 - m_2^2)}{(R-1)^2 m_1 m_2 [3x^2 m_1 m_2 - 4x(m_1 + m_2) + 4 + (Rm_2^2 - m_1^2)/m_1 m_2 (R-1)]} . \quad (9) \end{aligned}$$

More conventionally, we can introduce Z by

$$\Delta x/x = Z(\Delta R/R) = Z'(R/x) . (\Delta R/R)$$

$$\text{or} \quad \Delta a/a = Z \cdot \frac{\Delta(n_1/n_2)}{(n_1/n_2)} . \quad (10)$$

As a specific example of this result, let us consider the α_1, α_2 doublet of the (7, 5, 2) line produced by Mo radiation incident on tungsten. Here

$$h_1^2 + k_1^2 + l_1^2 = h_2^2 + k_2^2 + l_2^2 = 78,\ \lambda_1 = 0{\cdot}70926 \text{ Å} ,$$
$$\lambda_2 = 0{\cdot}71354 \text{ Å},\ a \simeq 3{\cdot}165 \text{ Å, and } R \simeq 2{\cdot}39 .$$

This implies if n_1/n_2 is known to one part in 10^2, a would be known to 1·6 parts in 10^4.

Of course, in an attempt to determine the accuracy of a particular measurement of a, we must include all systematic and random errors in our estimate of

$$\Delta(n_1/n_2)/(n_1/n_2) .$$

Fortunately, the two lines are fairly close together, hence their spectral profiles are similar. Thus, most of the systematic errors in measuring the two lines are in the same direction and of nearly the same magnitude. From this it can easily be shown that taking the ratio cancels the individual errors in n_1 and n_2 to first order.

I would like to thank Dr J. Karle and Dr H. Hauptman for continued interest and helpful discussions.

References

Černohorský, M. (1960). *Acta Cryst.* **13**, 822.

Rovinskij, B. M. & Kostjukova, E. P. (1958). *Kristallografija*, **3**, 383.

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The compound Li_2MgPb.*

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We have prepared the compound Li_2MgPb, determined its structure and melting point. Samples were prepared by melting together metallic elements of greater than 99·5% purity. Melting and thermal analysis were done on samples in a pure iron crucible in an argon atmosphere. Crystals, a centimeter on an edge, grew easily in a 300 g. sample which required about thirty minutes to freeze. The compound is brittle, has a metallic blue color, and tarnishes in a matter of minutes in laboratory air.

The measured and calculated weight percentages of the elements are, respectively: Li, 5·71 ± 0·06, 5·66; Mg, 9·99 ± 0·02, 9·91; Pb, 84·1 ± 0·3, 84·43. A congruent melting point of 859 °C. was measured for the compound. The true melting point of the pure compound is probably within 10 °C. of this value.

X-ray diffraction powder patterns showed this compound to have a face-centered cubic structure. We compare our proposed structure for this compound with Li_3Pb (Zalkin & Ramsey, 1956) and Mg_2Pb (Brauer & Tiesler, 1950*a*):

	Li_3Pb	Mg_2Pb	Li_2MgPb
a_0 (Å)	6·687	6·813	6·781
Positions*			
0, 0, 0,	Pb	Pb	Pb
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2},$	Li	Vacant	Mg
$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}$	2 Li	2 Mg	2 Li

* To all positions is added face-centering.

Since X-ray diffraction does not readily reveal light atom positions in this structure, we propose soon to carry out neutron diffraction. If the structure is as ordered as we suppose, we may look for disordering among the light element positions by electrical resistivity measurements. (The nuclear magnetic resonance adsorption line of the Li in the compound is sharp as it is in semiconducting Li_3Bi, whereas the line is broad in conducting lithium intermetallic compounds (Holder, 1960).)

The compound satisfies the criteria of Mooser & Pear-

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* This work was performed under the auspices of the U.S. Atomic Energy Commission.

son, 1957, for semiconductivity, and is seemingly isostructural with Li_2MgSn investigated by Laves (cited in Mooser & Pearson, 1957). The only other work on the Li–Mg–Pb system of which we are aware is that of Brauer & Tiesler (1950*b*) who showed that Mg_2Pb can take as much as 9·8 mole per cent Li_4Pb into solid solution.

We are indebted to Mr D. H. Wood for preparing one of the samples of the compound, to Mr V. G. Silveira for the powder photography, and to the Analytical group for chemical analysis.

References

BRAUER, G. & TIESLER, J. (1950*a*). *Z. anorg. Chem.* **262**, 319.

BRAUER, G. & TIESLER, J. (1950*b*). *Z. anorg. Chem.* **262**, 309.

HOLDER, B. E. (1960). This laboratory, personal communication.

MOOSER, E. & PEARSON, W. B. (1957). *J. Chem. Phys.* **26**, 893.

ZALKIN, A. & RAMSEY, W. J. (1956). *J. Phys. Chem.* **60**, 234.

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The variation of apparent bond lengths with temperature in molecular crystals.

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Atomic coordinates obtained from Fourier or least-squares calculations, in which the structure factors are calculated for atoms assumed to be undergoing *linear* anisotropic vibrations, will be in error if a molecule is undergoing *angular* oscillations (Cox, Cruickshank & Smith, 1955; Cruickshank, 1956*a*, 1961). In the simplest case an atom will appear too close to the axis of angular oscillation by roughly $\frac{1}{2}r\theta^2$, where r is its distance from the axis and θ^2 is the m.s. amplitude of angular oscillation. At temperatures above the characteristic temperature Θ_E, which is often about 50–100 °K. for the librations in molecular crystals (Cruickshank, 1956*b*), θ^2 will be roughly proportional to the absolute temperature. Thus, as the temperature falls below room temperature, the apparent displacement $\frac{1}{2}r\theta^2$ should decrease appreciably. Consequently the uncorrected bond lengths in a molecule such as benzene ought actually to *increase* as the temperature *falls*, provided that the intermolecular forces are too small to cause any appreciable change in the 'true' bond lengths.

Table 1. *The* CN *bond length in* $(CH_2)_6N_4$

Temperature (°K.)	Cell dimension (Å)	Radiation used	Uncorrected length (Å)	Rotational correction (Å)	Corrected length (Å)
298	$7·021 \pm 9$	Cu	$1·464 \pm 5$	0·014	1·478
		Mo	$1·465 \pm 2$		1·479
100	$6·931 \pm 8$	Cu	$1·474 \pm 7$	0·005	1·479
		Mo	$1·467 \pm 2$		1·472
34	$6·910 \pm 8$	Cu	$1·474 \pm 4$	0·002	1·476
		Mo	$1·475 \pm 1_2$		1·477

We have recently undertaken single crystal X-ray studies of $(CH_2)_6N_4$ at 298, 100 and 34 °K. in order to investigate the variation of vibration amplitudes with temperature and to interpret them by a lattice-vibration spectrum. The main results will be reported elsewhere, but the values found for the CN bond lengths at different temperatures are relevant here. The bond lengths and their e.s.d.'s derived from full-matrix least-squares calculations for the three temperatures and from the independent observations made with Cu and Mo radiation are shown in Table 1. These show fairly clearly that the uncorrected CN bond length does increase as the temperature decreases.

At 298 °K. the angular oscillation θ^2 about any molecular axis is found to be $43·1 \pm 2·0$ deg.², which corresponds to a characteristic temperature $\Theta_E = 64·5$ °K. The angular oscillations at the lower temperatures are $11·2 \pm 1·1$ deg.² at 100 °K. and $6·0 \pm 0·8$ deg.² at 34 °K.; these are close to those predicted with the above Θ_E. After application of the rotational corrections (Cruickshank, 1956*a*), the CN lengths given in the last column of Table 1 are obtained.† The results show that the corrected CN length is the same at all temperatures within experimental error and so provide direct evidence for the validity of this type of correction. Similar evidence from other crystals is of course desirable for further confirmation.

It may be added that the uncorrected C–N lengths obtained in the present work for 298 °K. are in satisfactory agreement with those obtained from new least-squares refinements of the previous X-ray (Brill *et al.*, 1939) and neutron data (Andreson, 1957), which are $1·457 \pm 5$ Å and $1·457 \pm 4$ Å. The weighted mean estimate of the corrected CN length derived from the various crystal-diffraction results is $1·476 \pm 0·002$ Å, where the e.s.d. has been set rather conservatively. This is in satisfactory agreement with the gas-phase electron-diffraction value of $1·48 \pm 0·01$ Å (Schomaker & Schaffer, 1947).

We are indebted to Prof. Dame Kathleen Lonsdale for some stimulating correspondence on this topic.

References

ANDRESON, A. F. (1957). *Acta Cryst.* **10**, 107.

BRILL, R., GRIMM, H. C., HERMAN, C. & PETERS, A. (1939). *Ann. Phys.* **34**, 435.

COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1955). *Nature, Lond.* **173**, 75.

CRUICKSHANK, D. W. J. (1956*a*). *Acta Cryst.* **9**, 757.

CRUICKSHANK, D. W. J. (1956*b*). *Acta Cryst.* **9**, 1005.

CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.

SCHOMAKER, V. & SCHAFFER, P. A. (1947). *J. Amer. Chem. Soc.* **69**, 1555.

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[†] The proper e.s.d.'s for the corrected lengths will be a little greater than those assigned to the uncorrected lengths, because these did not allow for the e.s.d.'s of the cell dimensions or for any error in the rotational corrections.