Short Communications

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Comments on the crystal structures of Ba_2Mg_{17} and Sr_2Mg_{17}.

By FREDERICK E. WANG, FRANK A. KANDA, CHARLES F. MISKELL and ADEN J. KING, *Chemistry Department, Syracuse University, Syracuse* 10, *N. Y., U.S.A.*

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Recently, Kripyakevich & Evdokimenko (1962) reported the structures of Ba_2Mg_{17} and Sr_2Mg_{17} which were formerly considered to be $BaMg_9$ and $SrMg_9$ by many authors (Nowotny, 1942; Klemm & Dinkelacker, 1947; Ray, 1947; Zeek, 1956) who investigated the Ba–Mg and Sr–Mg phase systems. The work of Kripyakevich & Evdokimenko, based on X-ray powder patterns, indicated Ba_2Mg_{17} and Sr_2Mg_{17} not to be isomorphous, contrary to some findings (Miskell, 1948), but to be isomorphous with Th_2Zn_{17} (Mokarov & Vinogradov, 1956) and Th_2Ni_{17} (Florio, Baenziger & Rundle, 1956) respectively. A previous report by Goldish & Marsh (1955) based on single-crystal data, considered $BaMg_9$ to be a disordered intermediate phase having a stoichiometric ratio of Ba(3·6):Mg(35). Apparently, the report of Kripyakevich & Evdokimenko and that of Goldish & Marsh are inconsistent. We wish to report here some of our results concerning the structure of Ba_2Mg_{17} based on single-crystal work, which may shed some light on this matter. The structure of Sr_2Mg_{17}, as suggested by Kripyakevich & Evdokimenko is isomor-

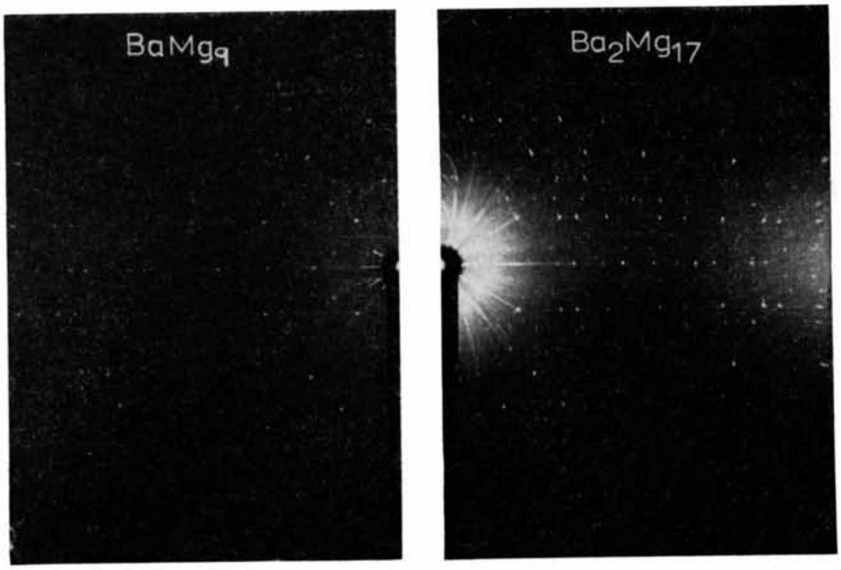

Fig. 1. 20° oscillation photographs of $BaMg_9$ and Ba_2Mg_{17}, rotated about the c^* axis.

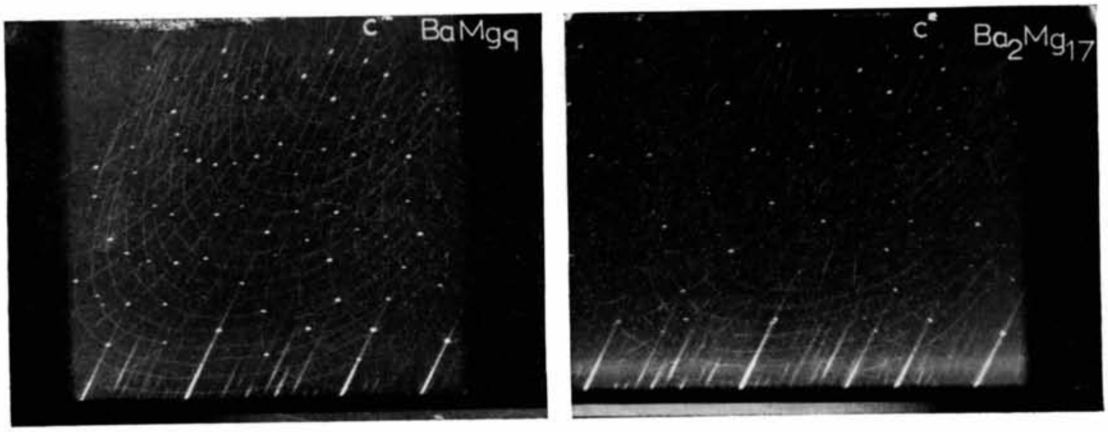

Fig. 2. Zero layer Weissenberg photographs of $BaMg_9$ and Ba_2Mg_{17}, rotated about the orthohexagonal axis.

phous with that of Th_2Ni_{17} (Florio, Baenziger & Rundle, 1956) and is a derivative structure af $CaZn_5$ (Haucke, 1940). However, we found Ba_2Mg_{17} to dissolve Mg substitutionally in its lattice. The substitution occurs only on the superlattice (here the $CaZn_5$ type lattice is considered to be the sublattice) and moreover only in a short range order. As partial evidence, we submit the 20° oscillation photographs of the single crystals obtained from samples corresponding to the atomic composition ratios of $BaMg_9$ and Ba_2Mg_{17}, rotated about the c^* axis, as shown in Fig. 1. The $3n(n = 0, 1, 2, 3, \ldots)$ layers are diffractions due mostly to the sublattice whereas the layers 1, 2, 4, 5, ... *etc* are solely due to the superlattice. It is seen that the diffraction due to the superlattice in $BaMg_9$ lacks a mirror plane of symmetry across the zero layer. Furthermore, when the equi-inclination zero-layer Weissenberg photographs for both $BaMg_9$ and Ba_2Mg_{17} were made (rotated about the orthohexagonal axis) as shown in Fig. 2, the following conclusions were reached. The superlattice of $BaMg_9$ does not have $6/mmm$ diffraction symmetry whereas Ba_2Mg_{17} shows $6/mmm$ diffraction symmetry for both the sub- and the super-lattice. The latter has been confirmed to be a derivative of a $CaZn_5$ type structure as suggested by Goldish & Marsh (1955) but it is not disordered and the c_0 axis dimension is 15·52 Å instead of 10·53 Å (a_0 being 10·61 Å). The substitutional solution of Mg atoms in the superlattice of Ba_2Mg_{17} thus creates a disorder which cannot be detected by powder patterns as in the case of the investigation by Kripyakevich & Evdokimenko. Our complete investigation of all the intermediate phases of R–X systems (where R = Sr, Ba and X = Li, Mg) is in its final stage and will be reported in the near future.

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Bond lengths and angles in pentaerythritol tetranitrate.

By James Trotter, *Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada*

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Very little information is available about the detailed structures of nitrate esters. Electron-diffraction investigations of fluorine nitrate and methyl nitrate (Pauling & Brockway, 1937) indicate non-planar molecules, while a more recent microwave study of methyl nitrate (Dixon and Wilson, 1961) suggests that the molecule is planar. The only X-ray analysis is that on pentaerythritol tetranitrate $C(CH_2O.NO_2)_4$ (Booth and Llewellyn, 1947); the authors noted three remarkable features of the molecular structure (Fig. 1): (i) the C(0)–C(1) bond (1·50 Å) is shorter than 1·54 Å; (ii) the C(1)–O(1) bond (1·37 Å) is considerably shorter than a normal single bond; (iii) the O(1)–N bond is of normal length. It might also be added that the N–O(2) and N–O(3) bonds seem to be abnormally long. No satisfactory explanation of these features can be given, and since no such abnormalities were noted in a recent analysis of *cis*-1,2-acenaphthenediol dinitrate (Mak & Trotter, 1963), the structure of pentaerythritol tetranitate has been reinvestigated to determine whether the abnormal distances are real.

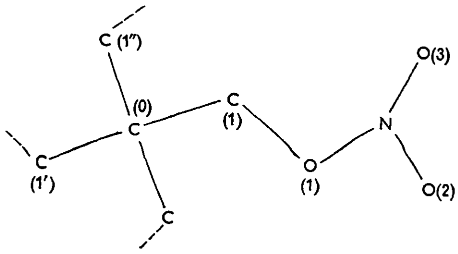

Fig. 1. Numbering of atoms in pentaerythritol tetranitrate.

Table 1. *Progress of refinement*

	R	$\Sigma w.\Delta F^2$
Initial coordinates	0·259	1129
1st least-squares cycle	0·180	654
2nd	0·160	529
3rd	0·153	525
4th	0·152	496
5th	—	—

Using Booth and Llewellyn's structure factor data (with the omission of the reflexions 021, 012, 121, 220, 222, 232, which might be affected by extinction), the scattering factors for C, N, O of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and an overall $B = 4{\cdot}5$ Å^2, the positional and isotropic thermal parameters and a scale factor were refined with a least-squares program for the IBM 1620 computer, written in FORTRAN, and with the general strategy suggested by Cruickshank (1961). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = |F_o|/10$ if $F_o < 10$ and $w = 10/|F_o|$ if $F_o \geqslant 10$. Refinement was complete in five cycles (Table 1), the final scale factor on Booth and Llewellyn's data being 1·079.