

## Short Communications

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**Comments on 'Parameter interactions and the ferroelectric mechanism in guanidinium aluminum sulfate hexahydrate' by Lingafelter, Orioli, Schein and Stewart.** By S. GELLER, *North American Aviation Science Center, Thousand Oaks, California, U.S.A.*

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Lingafelter, Orioli, Schein & Stewart (1966) have corroborated the results of our investigation on guanidinium aluminum sulfate hexahydrate (GASH). We wish now to examine additional claims made in their paper.

Lingafelter *et al.* say that we "have given no explanation of the source of the parameter interaction other than the statement" in our summary "that 'The numerous high correlations of pairs of parameters, apparently linked with the nature of the structure, appear to be a primary cause of prevention of convergence.'" They go on to say that in the footnote of my 1961 paper and in unpublished comments, I have stated my belief that the interactions are caused by the nearly triply-primitive nature of the structure. The first statement attributed to us is correct, while the second is incomplete. Considering the prior publication of the structure of the gallium isomorph (Geller & Booth, 1959) and my 1961 paper, there was no need to give any further details in the Geller & Katz (1962) paper; the statement made in the summary is sufficient.

In the earlier paper on the gallium isomorph, it was specifically pointed out that the first trial structure was obtained by 'Excluding the guanidinium ions,' assuming 'that the structure could be based on  $P\bar{3}m1$ .' Even a cursory examination of the parameters of both the gallium and aluminum isomorphs reveals this. The pairs of atoms 'nearly' related by a center at 000 are (see Table IV of the 1962 paper) O(V) and O(VI), O(IX) and O(X), O(VII) and O(VIII), O(III) and O(IV), O(I) and O(II), S(I) and S(II). Al(I) is held constant at 000, Al(II)'s are near  $\pm(\frac{1}{3}, \frac{2}{3}, 0)$ . C(I) is near  $0, 0, \frac{1}{2}$ , C(II)'s are near  $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ . In the guanidinium groups the  $x$  and  $y$  coordinates of the N atoms are almost exactly related by  $0, 0; \frac{1}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3} - (0, u; u, 0; \bar{u}, \bar{u})$  and the  $z$  parameters of the two nonequivalent N's are close. It should also be obvious that all groups of atoms need not be related by the same 'virtual' symmetry operations to be highly correlated.

Lingafelter *et al.* assert that the polar nature of the structure causes one class of correlations, two-thirds of which are between sulfur and other atom  $z$  parameters. That not fixing the Al(I)  $z$  parameter would alone not produce a unique solution is trivial. It would seem, however, that the fixing of this parameter should remove a large measure of the arbitrariness. Some correlations involving heavy atoms should still exist, and it is perhaps for this reason that such a large number involve the sulfur  $z$  parameters, but it is interesting that correlations of the Al(II)  $z$  parameter are all  $<0.4$ , while some involving only lighter atoms are  $>0.4$ . Further, in the BaTiO<sub>3</sub> case (Geller, 1961), in which the Ba position was fixed, one  $\rho$  for  $z(\text{O}_{II})-z(\text{O}_I)$  is large, 0.55, while those for  $z(\text{O}_{II})-z(\text{Ti})$  and  $z(\text{O}_I)-z(\text{Ti})$  are relatively small, 0.25 and 0.20 respectively. Thus the first

set of correlations to which Lingafelter *et al.* refer may have a somewhat different origin.

It will be noted in our Table X (Geller & Katz, 1962) that for 'related' atoms in special positions the  $z-z$  correlations are always higher than the  $x-x$ . For example, for S(I) and S(II), the  $z-z$  correlation is 0.90-1.00, while the  $x-x$  is 0.70-0.80. For O(I) and O(II), the  $z-z$  is 0.50-0.60, while the  $x-x$  is less than 0.4. For O(III) and O(IV),  $z-z$  is 0.80-0.90, while  $x-x$  is 0.60-0.70. For O(VII) and O(VIII), both are less than 0.40. I regret that I no longer have these results, but the trend suggests that they differ by about 0.20, which may be roughly the part resulting from the polar nature of the structure. Thus it appears that one must consider the manner in which each atom contributes to the structure factors and see in turn how these affect the correlations before attempting to make assertions as to their origin.

As to the correlations in Table 4 of Lingafelter *et al.*, these may be caused by the nonorthogonality of the cell. According to Templeton (1959), the values for each  $x, y$  pair should be 0.5, provided that no correlation exists between coordinates of the different atoms. Our values for these correlations (see Table X of Geller & Katz, 1962) are actually all  $<0.5$ . One might have expected these to be larger because the atoms lie nearly in virtual planes of symmetry (see also Geller, 1962). But the numerous interactions do cause strange results. For example, consider our results for the correlations of the positional parameters for O(IX) and O(X) related by the near center of symmetry (see Table X of Geller & Katz, 1962): we obtained for  $x-x$ ,  $<0.4$  and for  $y-y$ , 0.7-0.8. For the other set of oxygen atoms in general positions, O(V) and O(VI), the values were  $x-x$ ,  $<0.4$ ,  $y-y$ , 0.6-0.7. Yet examination of our Table VI leaves little doubt that the two sets of atom coordinates are similarly related; that is, one might expect the  $x-x$  and  $y-y$  correlations to be very nearly the same in both cases. Again, in a situation as complex as this one, assertions are unwarranted.

Lingafelter *et al.* have chosen a near-center different from the one I have discussed to which to relate their third group of correlations. But examination of our tables of correlations and our parameters bring out the same relationships. They then show also that there is a third near-center. But both lead to the nearly triply-primitive structure (which contains the obvious near-center I have discussed) which accounts for all the correlations of both the Lingafelter *et al.* near-centers; it is rather difficult to see how the case could be otherwise as suggested by Lingafelter *et al.*

In our 1962 paper, we made no speculations on the ferroelectric behavior of GASH and its isomorphs. This is a complex matter, and other types of measurements have

not really revealed strong evidence regarding the mechanism of polarization reversal. Lingafelter *et al.* claim that they have given a mechanism. While they speculate on the geometrics, no physical basis is given.

How, for example, can an electric field perpendicular to the plane of a guanidinium ion cause it to rotate? Further, it is required that one of two equivalent guanidinium ions rotate and become equivalent to the unique one, while the other (of the originally equivalent pair) becomes unique.

I have discussed these points with R. P. Futrelle and W. F. Hall of our laboratory. It is possible that rotations could take place. For example, suppose the groups above and below the guanidinium ions carry negative charges. The guanidinium ion carries a positive charge distributed with threefold symmetry in its plane. It is closer to one negative group than to the other and is in its equilibrium position. Imposition of an electric field strong enough to move these negatively charged groups might move the group which was originally further from the guanidinium ion closer to it, and the one that was closer, further from it. Thus the new equilibrium position could involve a rotation of the guanidinium ion. This much (though not given by Lingafelter *et al.*) is acceptable.

However, it is required that one of two equivalent guanidinium ions rotate. It may be argued that as soon as one of these rotates, all others in the *same* aspect rotate, while the remainder stay essentially in their original positions. Such an argument does not appear to be tenable. It would seem that the probability for rotation would be equal for the two equivalent guanidinium ions (and there does not seem to be any obvious qualitative reason that the unique one should not rotate also). This implies, then, that the *original* GASH crystal should be multiply-twinned, that is, that domains should be present with each of the possible sets of orientations.

Consideration of this possibility leads to the conclusion that the (+, +) and (+, -) (see Geller & Katz, 1962)

guanidinium ion configurations should be equally probable. Our calculations (Geller & Katz, 1962), to some extent, included a check of this hypothesis. The (+, -) configuration was preferred. As we have pointed out (Geller & Katz, 1962), the exact (+, +) configuration makes no contribution to intensities of reflections  $hk \cdot l$  with  $h-k \neq 3n$ . However, because both configurations are equally probable, it is unlikely that the preferred one would have been the (+, -) one (almost exactly) if such disorder actually existed in the crystal. In fact, we also checked a configuration in which the two equivalent guanidinium ions were rotated  $30^\circ$  from their positions given in our Table IV; the calculations showed that these were unlikely. Thus the suggestion made by Lingafelter *et al.* with regard to the polarization reversal lacks a firm foundation.

Unfortunately, despite the publication of a number of papers on GASH, there is little evidence regarding the switching mechanism. Holden, Merz, Remeika & Matthias (1955) pointed out that while they obtained no details regarding it, they did obtain some evidence (which they gave) that it is principally the same as for  $\text{BaTiO}_3$ , that is, 'mainly a nucleation problem of domains'. However, as far as I know, no further evidence substantiating this conclusion has been published.

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**A measurement of the dispersion correction.** By R. J. WEISS, *Materials Research Laboratory, U.S. Army Materials Research Agency, Watertown, Massachusetts, U.S.A.*

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Recently Chipman & Jennings (1963) were able to measure the dispersion correction  $\Delta f'$  in the inert gases Ne, Ar, Kr and Xe by an extrapolation of the absolute scattering factor  $f$  to  $\sin \theta/\lambda = 0$  where  $f = Z + \Delta f'$ . While it would have been possible to calculate  $\Delta f'$  from measured values of the absorption coefficient over all wave lengths, such values were not available in sufficient accuracy for Chipman & Jennings to determine whether their measured values of  $\Delta f'$  were correct. In none of the four cases was the dispersion correction more than  $\sim 2\%$  of  $Z$  at the Mo  $K\alpha$  radiation employed. We therefore considered it worthwhile to make an *absolute* determination of  $\Delta f'$  in a case where the contribution is considerably greater than  $2\%$ .

The measurements were made by comparing the ratio in reflection of the 440 scattering factor at Ge  $K\beta$  of a perfect crystal of germanium to the 440 scattering factor of a perfect crystal of silicon, both crystals having been previously measured on an absolute basis (DeMarco & Weiss, 1965) at Mo  $K\alpha$  where  $\Delta f'$  is small. At Ge  $K\beta$  ( $\lambda = 1.129 \text{ \AA}$ ,  $\lambda/\lambda_K = 1.011$ )  $\Delta f'$  comprises over  $30\%$  of the total scattering factor

for the 440 in Ge but only  $\sim 1\frac{1}{2}\%$  to the 440 in silicon. A theoretical value of  $\Delta f' = +0.1$  was employed for silicon, an error of  $\sim 50\%$  in  $\Delta f'$  only contributing an uncertainty of  $\frac{1}{2}\%$ .

A Norelco fluorescence unit was employed to produce the Ge  $K\beta$  by fluorescence of germanium. Under identical conditions the integrated reflecting power was made of the Si 440 and Ge 440 reflections over a sufficiently large angular range ( $\Delta 2\theta = 6^\circ$ ) to ensure that the entire  $K\beta$  was diffracted. The thermal diffuse scattering correction was made as in the previous absolute measurements with Mo  $K\alpha$ . By making several runs and interchanging crystals the beam power appeared constant within the statistical error of  $\sim 1\frac{1}{2}\%$ . The measured value of  $\Delta f'$  for Ge  $K\beta$  on germanium was determined to be

$$\Delta f' = -4.66 \pm 0.3.$$

In order to compare this value with theory we employed the values of the oscillator strengths  $g$  calculated by Cromer (1965) with the relativistic Dirac-Slater wave functions. We