118. Are Ionic Solids Really Built of Ions? New Evidence from X-Ray Diffraction

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A new, accurate, low-temperature X-ray analysis of lithium tetrafluoroberyllate, Li_2BeF_4, reveals that the charge density in this crystal is better represented as a superposition of spherical neutral-atom charge distributions than as a superposition of ionic charges. The two distributions are so similar that they are hardly distinguishable by examination of the total charge density in real space. However, the two models are clearly differentiated by analysis of the weak low-order reflections; the measured intensities are reproduced better by calculations based on neutral-atom scattering curves. This result may appear to run counter to the current conventional wisdom concerning ionic solids, but it is unlikely to have any important practical consequences.

Although many solids, such as LiF, are conventionally described as ionic, an experimental proof that they are really built from ions is hard to come by. In fact, the ionic and covalent descriptions are not so very different. As *Slater* [1] has pointed out, the difference in charge distribution between the superposition of the neutral atoms and the superposition of the ions is small and subtle, and difficult to determine by examination of the total density. The densities of individual neutral atoms and corresponding ions only become appreciably different at such large distances from the respective nuclei that in a condensed phase, where densities of neighbouring atoms overlap, this diffuse difference density cannot be unequivocally assigned to one atom or another. At these large distances, the density associated with a given atom may be quite small, but the contribution of the spherical shell to the integrated charge may be considerable.

The possibility of solving the problem in reciprocal space would appear to be just as unpromising. 'Any attempt to determine the state of ionisation of the atoms in a crystal by means of measurement of the atomic scattering factor is likely to fail, since ... the curves will differ appreciably only at (scattering) angles for which no spectra exist' [2]. This authoritative though pessimistic conclusion has been reiterated many times, most notably, perhaps, by *Bijvoet* and *Lonsdale* [3] in their discussion of earlier claims to have determined the state of ionization of LiH. The point is that the scattering powers of neutral atoms and their corresponding ions differ appreciably only in a small region of reciprocal space close to the origin.

Nevertheless, the scattering factors of charged and uncharged atoms do differ appreciably at small scattering angles and are not quite identical even at larger ones. Thus, *James*'s conclusion may not necessarily be valid, especially for crystals with unit cells large enough to produce diffracted spectra at small $\sin\theta/\lambda$ values ($<$ *ca.* 0.2 Å^{-1}) and provided the structure amplitudes can be measured with very high accuracy. Over the years many attempts to overcome these problems have been made (*e.g.* [4]). Other aspects of the difficulties of assigning atomic ionicities in solids have been reviewed recently [5].

The Lithium Tetrafluoroberyllate Structure. – We have recently taken up this problem again in connection with a re-examination of the charge density in Li_2BeF_4. In this crystal structure [6], each Li- and Be-atom is surrounded by a tetrahedron of F-atoms, and each F-atom has one Be- and two Li-atoms as nearest neighbours; chains of interlinked tetrahedra run along the *c* axis of the trigonal cell, space group $R\bar{3}$ *(Fig. 1)*. The crystal structure and lattice energy can be reproduced extremely well by force-field calculations [7] based on a purely ionic model, *i.e.* by assuming the crystal to be built from the simple ions Li^+, Be^{2+}, and F^-, although *McGinnety* [8] considers that this picture is to be supplemented by appreciable covalent interactions in the Be–F bonds and by smaller, but not negligible, interactions in the Li–F bonds.

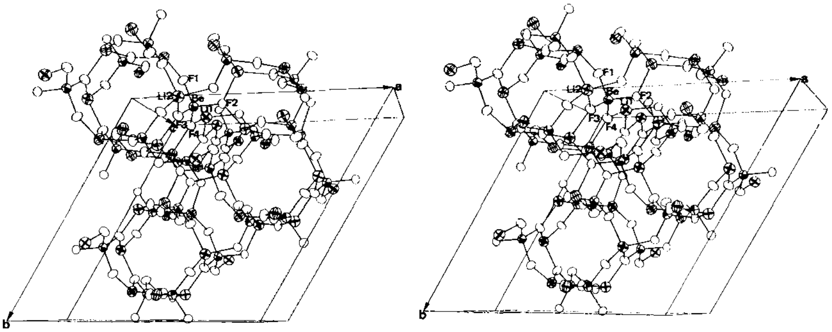

Fig. 1. *Stereoview of the crystal packing of Li_2BeF_4*. The atomic displacement ellipsoids are based on data from crystal I measured at 81 K and are drawn at the 98% probability level.

With 6 formula units in the primitive rhombohedral cell, the cell volume is 455 $Å^3$, nearly 30 times larger than that of the primitive cell of LiF, say. Indeed, for Li_2BeF_4 there are some 40 reflections in the low-order region with $\sin\theta/\lambda < 0.25$ $Å^{-1}$ where there are still differences between the scattering powers of the respective neutral atoms and ions. From new, low-temperature measurements, we now find that the structure is better represented as a superposition of neutral atoms than as a superposition of free-ion electron densities.

Preliminary Observations. – Our attention was first directed towards the Li_2BeF_4 structure by the claim, based on a room-temperature X-ray analysis, that appreciable bonding density (up to 0.4 e·$Å^{-3}$) could be observed in a difference $(F_o - F_c)$ *Fourier* synthesis for the Be–F bonds but not for the Li–F bonds [9]. We were dubious, since we had just previously observed only much weaker bonding density (*ca.* 0.10 e·$Å^{-3}$) in the C–F bonds of tetrafluoroterephthalonitrile in a low-temperature (100 K) X-ray study [10]. New, more extensive, and more accurate measurements were then made for Li_2BeF_4 at 81 K, as described below. Atomic coordinates and anisotropic *Gaussian* displacement parameters were estimated by least-squares analysis for two models, one consisting of spherical neutral atoms, the other of the conventional ions [11]. Both models led to essentially the same results, the coordinates being close to those of the room-temperature structure [6] [9], the displacement parameters being reduced by 40–60%. Also, the low-temperature difference maps based on the two pro-crystal models did not differ in any essential respect, both being quite flat and featureless (nothing above 0.1 e·$Å^{-3}$), in contrast to the results of the room-temperature study [9].

Since the conventional R factors ($R = \Sigma|F_o - F_c| / \Sigma|F_o|$) for both models were almost identical and as low as could be expected from the quality of the data (0.015, including all 6345 measured reflections), the analysis seemed to provide yet another confirmation that the state of ionization of the atoms could not be determined by X-ray diffraction. However, scrutiny of the weak low-order reflections led to a different conclusion: for 11 such reflections ($F_o < 4$, $\sin\theta/\lambda < 0.25$ Å^{-1}) the R factors were 0.043 for the neutral atom model and 0.125 for the ionic, a difference striking enough as to suggest that the matter was at least worth pursuing further.

Experimental. – All X-ray measurements were made with an *Enraf-Nonius CAD4* diffractometer equipped with graphite monochromator (Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å) and a modified *Enraf-Nonius* gas-stream low-temperature device. The temp. of the N_2 gas stream was kept constant at 81 K (±0.5 K) during the experiments.

Two sets of measurements were made, with different crystal specimens. With crystal I (diameter ~ 0.42 mm) all 6345 independent reflections out to $\sin\theta/\lambda = 1.36$ Å^{-1} were measured, mostly in all symmetry-equivalent orientations. These are the measurements we have used to determine the atomic parameters and the charge-density difference maps. Crystal II (diameter ~ 0.22 mm) was used to measure the low-order reflections (out to $\sin\theta/\lambda = 0.48$ Å^{-1}). At 81 K the unit cell dimensions are $a = b = 13.281(2)$ Å, $c = 8.888(1)$ Å.

Low-order reflections are particularly sensitive to certain kinds of experimental error, such as extinction, multiple reflection and higher harmonic contributions, the effects of which depend on crystal size and perfection as well as other factors. The extinction error can be estimated by refining a suitable correction factor in the least-squares analysis or by making measurements with crystals of different sizes. We used both methods and made appropriate corrections. In any case, as expected, the extinction correction was found to be relatively unimportant for the weak reflections. We therefore picked 22 weak reflections with $\sin\theta/\lambda < 0.25$ Å^{-1} that were sensitive to the choice of model and set out to measure these as accurately as possible with crystal II.

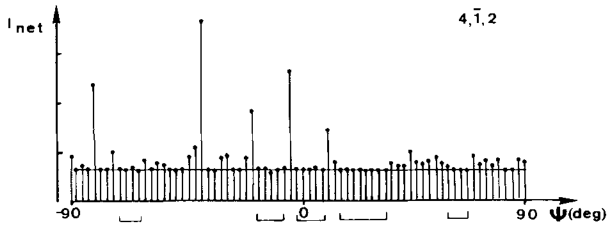

Fig. 2. *Azimuthal intensity profile showing simultaneous diffraction spikes for the weakest low-order* Bragg *reflection of Li_2BeF_4*

Multiple reflection can be detected by analyzing the azimuthal intensity profile of a reflection, *i.e.* by rotating the crystal about the diffraction vector **H** and measuring the intensity at different angular settings. *Fig. 2* shows the azimuthal profile for a weak low-order reflection; the intensity due to multiple reflection occurs as sharp spikes in the profile. When the averaging of the individual intensity measurements is limited to the indicated flat regions of the profile, the internal agreement among symmetry-equivalent reflections is better than 1%. Care was also taken to reduce intensity errors due to higher harmonic contributions as far as possible. Full details will be published elsewhere.

The Crystal is Built from Neutral Atoms. – The *Table* shows a comparison of measured and calculated intensities based on the two extreme models for the 22 weak low-order reflections. The atomic coordinates and displacement parameters for the two models were estimated from two separate least-squares refinements, including all measured reflections (out to $\sin\theta/\lambda = 1.36$ Å^{-1}, crystal I). The coordinates are practically identical (within 10^{-4} Å). For the displacement parameters, the largest difference on going from the neutral to the ionic model is a decrease of *ca.* 2.5×10^{-4} Å^2 in the Be parameters; the Li parameters decrease by about 1×10^{-4} Å^2, and the F parameters change in the opposite sense but only by 0.4×10^{-4} Å^2. From the *Table*, it is obvious that of the two extreme models the neutral atom one is in better agreement with the observations.

Table. *Measured and Calculated Intensities for the 22 Weak Low-Order Reflections for the Neutral Atom and Ionic Models.* The observed values are from crystal II, the calculated ones are based on the atomic parameters obtained with the full data set from crystal I and include an isotropic extinction correction, estimated for crystal II.

h	*k*	*l*	$\sin\theta/\lambda$	*I* (obs.)	*I* (calc.) Neutral	ΔI	*I* (calc.) Ionic	ΔI
1	0	1	0.071	977	933	44	920	57
1	1	0	0.075	91095	90928	167	93124	–2029
2	0	–1	0.104	720	748	–28	546	174
1	0	–2	0.121	46337	46331	6	41221	5116
1	2	–1	0.128	77364	77501	–137	67563	9801
2	1	1	0.128	54495	54252	243	47929	6566
2	0	2	0.142	10028	9777	251	9108	920
2	1	–2	0.161	13887	13636	251	12461	1426
1	2	2	0.161	13557	13461	96	11938	1619
3	1	–1	0.167	594	620	–26	367	227
1	3	1	0.167	10972	10947	25	9622	1350
0	0	3	0.169	615	489	126	551	64
4	0	1	0.183	8840	8441	399	8912	–72
3	1	2	0.193	177	180	–3	158	19
1	3	–2	0.193	80	76	4	52	28
3	2	1	0.198	3184	3043	141	3304	–120
2	3	–1	0.198	821	779	42	752	69
4	0	–2	0.207	175	161	14	54	121
2	3	2	0.220	11099	10774	325	11809	–710
4	2	–1	0.237	2805	2729	76	2949	–144
2	4	1	0.237	146	176	–30	257	–111
2	0	–4	0.241	322	287	35	268	52

Of course, the charge density in the crystal need not correspond exactly to either extreme. As a first approximation towards a more realistic model, we assume that the scattering factor for each type of atom can be represented as a linear combination of the scattering factors of the neutral and charged species, *i.e.*

$$f(\mathrm{A}) = p_{\mathrm{A}} f(\mathrm{A}^{\mathrm{o}}) + (1 - p_{\mathrm{A}}) f(\mathrm{A}^{\mathrm{ion}})$$

where the condition $2p(\mathrm{Li}) + 2p(\mathrm{Be}) = 4p(\mathrm{F})$ is required to preserve electric neutrality of the crystal as a whole. The *p* coefficients may be determined, in principle, by least-squares

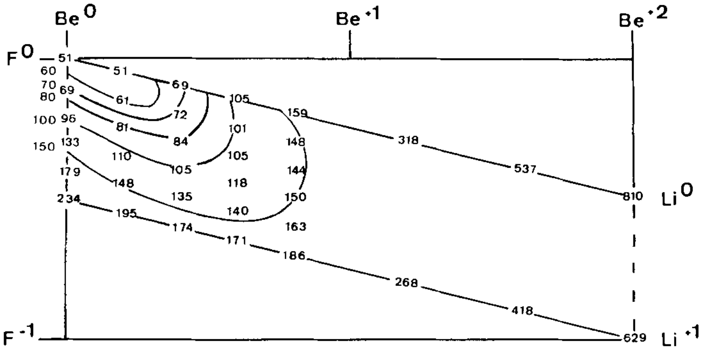

Fig. 3. *The quantity* $Q = \Sigma w(I_o - I_c)^2$ *for the 22 weak low-order reflections* (data from crystal II) *as a function of the ionicity coefficients* p *where the atomic scattering curves are represented as* $f(A) = p_A f(A^o) + (1 - p_A) f(A^{ion})$. The constraint condition $2p(\mathrm{Li}) + 2p(\mathrm{Be}) = 4p(\mathrm{F})$ is imposed to preserve overall electric neutrality.

analysis. What we have done is to calculate the quantity $Q = \Sigma w(I_o - I_c)^2$ summed over the 22 low-order reflections as a function of the p coefficients and plot the result, which is shown in *Fig. 3*. There is a pronounced minimum in Q and it occurs at or very close to the neutral atom structure. Minor changes in the refinement procedures could easily alter the details of the Q plot (*e.g.*, p(Li) is clearly less well determinable than p(Be)) but they could hardly change its main features. Thus, the analysis of the low-order reflections leaves little doubt that the charge density in Li_2BeF_4 is better represented as a superposition of neutral atoms than as a superposition of ions.

However, it must be stressed that both models fit the experimental charge density very closely, as shown by the low values of the R factors or by the very flat and featureless difference maps obtained with both models. Indeed, to see any detail whatsoever in the difference maps, it is necessary to plot them with contour levels much more closely spaced than the usual 0.1 or 0.075 e · $Å^{-3}$ intervals. As seen in *Fig. 4*, both models still lead to weak peaks of about 0.07 e · $Å^{-3}$ along the Be–F bonds and even weaker ones of up to 0.03 e · $Å^{-3}$ along the Li–F bonds (*cf.* peak heights of about 0.10 e · $Å^{-3}$ for C–F and 0.4–0.5 e · $Å^{-3}$ for C–C bonds in tetrafluoroterephthalonitrile in a roughly comparable analysis [12]). Thus, although the difference densities for both models are low they still show obviously systematic, common features that point towards a slight degree of covalent character in the Be–F bonds and possibly also even in the Li–F bonds, in agreement with *McGinnety*'s suggestions [8]. These features should be defined more clearly in the static deformation density based on an atom-centred multipole expansion [13].

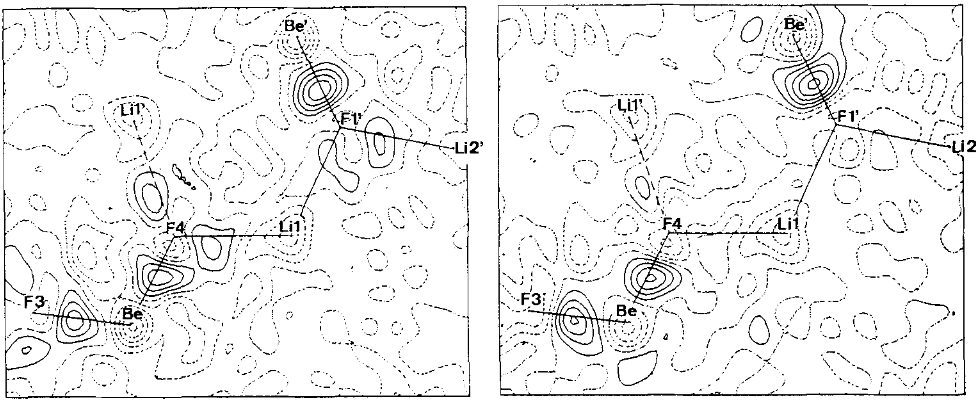

Fig. 4. *Electron-density difference maps calculated with all 1831* ($F_0 - F_c$) Fourier *coefficients out to* $\sin\theta/\lambda = 0.9$ $Å^{-1}$ (crystal I, 81 K). The map on the left is based on the neutral atom pro-crystal model, the one on the right is based on the ionic model. In both maps contour levels are drawn at intervals of 0.015 e · $Å^{-3}$, full lines for positive density, dashed for negative and zero. The standard deviation of the difference density, estimated as $[2\Sigma\sigma^2(F_o)]^{1/2}/V$, is 0.005 e · $Å^{-3}$.

Summary and Conclusions. – We have shown that the charge density in Li_2BeF_4 is described either as a superposition of spherical neutral atom densities or as a superposition of free-ion densities. Difference maps based on the two pro-crystal models are hard to tell apart. Both show very slight density accumulations along the Be–F bonds and still weaker ones along the Li–F bonds; otherwise they are practically featureless.

Nevertheless, when attention is concentrated on the low-order reflections, comparison of observed and calculated intensities leaves no doubt that the neutral atom model is in better accord with the observations. What this means is that the charge density in the diffuse regions far from the nuclei is better represented by the superposition of outer tails of spherical distributions centred at the Li- and Be-atoms than by the tails of F-centred distributions.

Although the difficulty of distinguishing between the ionic- and neutral-atom models has been known for many years, the former seems to have established itself as part of the conventional wisdom in chemistry and solid-state physics. Even in quite recent studies of alkali halides such as LiF [14] [15], the problem is avoided by taking the ionic model for granted; the experimental data were then interpreted as 'indicating that the negative ions are slightly compressed and the positive ions slightly expanded with respect to the free-ion charge densities'. The main reasons for the widespread acceptance of the simple ionic model are its ease of application and its remarkable success in calculating cohesive energies of many types of crystals. However, since the charge distribution of the ionic model is extremely close to that of the neutral atom model, the two distributions must correspond to very similar energies. Thus, the cohesive energy calculated for an ionic model with integral charges will be close to the correct result, even if the charge distribution is closer to that of neutral atoms [16]. The fact that it is easier to calculate many properties of solids with integral charges than with atomic charge distributions certainly makes the ionic model more convenient, but it does not necessarily make it more correct.

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