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## Can the long-range behaviour of interatomic forces be derived from phonon data?

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**Abstract.** The difficulties of determining the range of the interatomic forces when only the experimental phonon frequencies are known are discussed. It is shown that in crystals with only one ion per unit cell the range can be deduced from the isotropic frequencies using standard statistical procedures. Results are presented for potassium.

Interatomic force constants (FCS) are, in principle, deducible from experimental phonon data. In practice, however, there are many problems. It is well known (Leigh *et al* 1971, Szigeti 1971) that there are several sets of FCS that fit the phonon frequencies alone, so to deduce the actual FCS we need to know the phonon eigenvectors as well. If we only know the phonon frequencies it is not obvious how to proceed.

Any chosen finite set of nearest-neighbour (NN) FCS can be fitted uniquely to these frequencies using a least-squares procedure (see, for example, Cowley *et al* 1966). There are however, many different such sets, e.g. the range of the FCS can be varied and, for a given range, there are many different sets—the set of all FCS, the set of two-body FCS, the set of central FCS etc. With any set of FCS so obtained at least two questions need to be answered:

- (i) Are the FCS so obtained a reasonable approximation to the actual FCS?
- (ii) How do we determine the actual range?

A fitting procedure is only reasonable provided the forces decrease fairly rapidly with distance. For this and for general reasons we would like to know how the forces vary with distance. We thus need to know how well the data will allow us to find the variation of the FCS with distance.

This paper is mainly concerned with this problem and with the range of the forces, i.e. the second of the questions, (ii). Some comments about (i), however, are relevant. For clarity and ease we concern ourselves only with crystals with one ion per unit cell. The experimental information usually available comprises the phonon frequencies along certain symmetry directions. Suppose there are  $n_j$  FCS describing the forces between the ion at the origin and the ion at  $R_j$ . In general  $n_j = 9$ . For close NNS, symmetry often reduces the magnitude of  $n_j$  but  $n_j$  is never less than two. Although assumptions (e.g.

central forces) are often made there is no *a priori* way of choosing which of these  $n_j$  FCS is more important. So we write  $N$  as  $N_J$  where

$$N \equiv N_J = \sum_{j=1}^J n_j \quad (1)$$

where  $J$  is the furthest NN. Yet to keep all the FCS causes problems: for example this often means there are more parameters than can be determined by the data. In an earlier paper (Ball and Hajaij (1988), hereafter referred to as I) we presented a procedure that, given  $J$ , provided a better way of deriving FCS from the experimental phonon frequencies and of finding out which FCS are important. In fact it overcame, in crystals with one ion per unit cell, many of the difficulties discussed by Szigeti (1971).

Nevertheless that procedure did not determine  $J$ . In this paper we explain how that procedure leads to a simple determination of the range, i.e.  $J_{\max}$ , the maximum value of  $J$ , that the experimental information will allow us to use.

This question cannot be answered easily when fitting to all modes because standard statistical procedures, i.e. the  $F$ -test, are designed to test situations in which the number of parameters can be altered one at a time. If we try to fit all the frequencies we have to alter  $n_j$  parameters each time.

This problem is overcome in the procedure presented in I, because we consider the isotropic frequencies. An isotropic frequency  $\nu_i(\mathbf{q})$  for a particular wavevector  $\mathbf{q}$  is given by

$$3\nu_i^2 = \sum_m \nu_m^2 \quad (2)$$

where the summation is over all modes. In this procedure we choose  $J$  isotropic NN FCS and fit these to the isotropic frequencies along the symmetry directions. There is only one isotropic FC between any two ions. This has two consequences: firstly, it means that the isotropic FCS can be uniquely determined, i.e. there are none of the difficulties that Szigeti (1971) found and, more importantly for the present discussion, it means that  $J$  can, in general, be altered by one (except where there are two inequivalent ions at exactly the same distance from the origin). Thus the  $F$ -test can be used to determine  $J_{\max}$  for the isotropic FCS.

In principle the results of using the  $F$ -test in this way only tell us about the measurable range of the isotropic forces. They, however, arise solely from the rigid-ion part of the pseudo-atoms (Ball 1975) and can be considered as being derived from the 'rigid-ion interatomic potential'  $\varphi(\mathbf{R})$  (see I). Thus  $J_{\max}$  virtually determines the measurable range of  $\varphi(\mathbf{R})$ . This is a very useful piece of information, as the resulting forces are usually the only significant ones, because the forces that arise from the deformation part of the pseudo-atoms are often negligible.

We have tested the procedure on potassium so that we could look at the results we got in I and see if those conclusions needed modification. We write

$$F_J = (S_J - S_{J-1})/[S_J/(N_0 - J - 1)] \quad (3)$$

(Chatfield 1970), where  $N_0$  is the total number of measured isotropic frequencies and  $S$  is the least-squares remainder (see I).

We performed calculations for  $J = 4, 5, 6$  and  $7$ . The results are given in table 1. They clearly show that  $J_{\max} = 5$ , which means that the experimental data are only sufficient to tell us what the five NN FCS are. The further FCS are too small for us to be able to ascertain.

**Table 1.** Isotropic force constants ( $\text{dyn cm}^{-1}$ ), least-squares remainders  $S$ , and resulting values of  $F$  for potassium for various values of  $J$ . (Please note that the values of the FCS published in I for  $J = 6$  were incorrect due to a program error.)

$J$	4	5	6	7
$T_1$	715.95	717.24	716.84	715.97
$T_2$	150.81	132.13	132.53	131.50
$T_3$	-14.42	-25.81	-25.30	-26.10
$T_4$	9.47	8.85	8.04	11.15
$T_5$	—	18.71	18.31	19.69
$T_6$	—	—	-1.77	2.22
$T_7$	—	—	—	-2.12
$S$	0.15490	0.11793	0.11775	0.11208
$F$	—	8.15	0.04	1.21

As we saw in I a screened form for  $\varphi(\mathbf{R})$  did not fit the results and that a form involving Friedel oscillations seems more plausible. The fact that we can only ascertain FCS out to five NNS means that we cannot with the present experimental results determine the long-range nature of  $\varphi(\mathbf{R})$  very well. Whether there are Friedel oscillations in the interatomic forces remains an open question; they still increase from a negative value for  $J = 3$  to a positive value at  $J = 4$ , a larger value for  $J = 5$ , and then become rather small, i.e. not measurable at  $J = 6$ . The results here mean that the data are insufficient to determine the existence of Friedel oscillations. The FCS do, however, decrease rapidly with distance showing that a fitting procedure is permissible.

The procedure we have suggested here seems reasonably successful. Nevertheless there are three features that could be improved. The first is that the FCS could change as  $J$  changes. This is because it is necessary for translational invariance to be satisfied so that the expansion functions for the frequencies are not orthogonal (Ball and Hajajj 1981). The second is that, if there are Friedel oscillations, there could be two consecutive FCS that are small, say at  $J = M + 1$  and  $J = M + 2$ , followed by one that is measurable for  $J = M + 3$ . The  $F$ -test would tell us to stop at  $J = M$ . The third is that it would be useful to have some errors on the FCS. All these problems need further investigation.

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