PHYSICAL REVIEW B, VOLUME 63, 174302

Influence of phonons on the pair distribution function deduced from neutron powder diffraction

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(Received 3 August 2000; published 12 April 2001)

The widths of the peaks in the pair distribution function (PDF) contain information on the phonons of a material. At large interatomic distances r the width of the peaks is fully determined by the thermal parameters. For low r, however, correlation effects reduce the width significantly, depending on the shape of the phonon dispersion curves. We have studied the sensitivity of the PDF with respect to the phonons by means of computer simulations based on various lattice dynamical models. The peak widths were calculated both in the one-phonon approximation as well as by a real space approach using displacement correlation functions. Exemplary results are presented for Ni, Rh, Nb, Ge, and CaF_2. We find that the PDF is rather insensitive to details in the phonon dispersion curves. Therefore, there is little hope to extract more information on the lattice vibrations from an experimental PDF than is contained in the thermal parameters. This finding contradicts a claim recently made by Dimitrov, Louca, and Röder [Phys. Rev. B **60**, 6204 (1999)].

DOI: 10.1103/PhysRevB.63.174302 PACS number(s): 63.20.Dj, 61.12.Ex

I. INTRODUCTION

The energy-integrated scattering law $S(Q)$ determined in a neutron powder diffraction experiment contains information both on the structure and on the dynamics of the material. Usually, the data are evaluated by the Rietveld method or a related one, whereby the inelastic part of the spectrum is treated as a background which is described by a suitably parametrized smooth function. Nevertheless, the results of such an analysis still contain information on the dynamics in the form of thermal parameters U, also denoted dynamical mean square displacements.[2] In the case of multiatomic compounds, partial thermal parameters U_i are related to the dynamics of individual atoms. In principle, even more detailed information on the dynamics can be obtained by extracting direction-dependent thermal parameters, although the orientational averaging in a powder experiment makes it rather difficult to determine the angular dependence of the thermal parameters with sufficient precision.

The Rietveld method requires data for a rather limited Q range only. With the advent of pulsed neutron sources, it became possible to collect data for a very large range of momentum transfer (of the order of $Q<40\,1/\text{Å}$) which allows one to use a different data evaluation technique, i.e., the computation of the pair distribution function (PDF). This technique makes use of the full information contained in the scattering law, including the inelastic part. Consequently, it can be hoped to gain more detailed information on the dynamics than just thermal parameters. Recently, Dimitrov, Louca, and Röder[1] claimed that comparing the experimental PDF with theoretical calculations based on standard interatomic potentials and the crystal symmetry allows one to reconstruct the phonon dispersion curves with astonishing precision, at least for fairly simple systems. This procedure (dynamics from powder diffraction) was implemented for two materials, a simple metal (fcc Ni) and an ionic crystal (CaF_2). In view of the complex and implicite data analysis it is virtually impossible to assess the validity of this claim without performing further calculations in order to study the sensitivity of the PDF with respect to the shape of the phonon dispersion curves. For this reason, we have carried out a systematic study of the PDF of some simple systems with respect to the lattice dynamics. We will show the reader in what way the PDF is determined by the elastic and inelastic parts of the neutron spectrum and what might be reasonably hoped to be learned from an experimental PDF determined with the use of a state-of-the-art technique. Exemplary results will be presented for Ni and CaF_2 and also for fcc Rh and bcc Nb in which the force field is more complex than in Ni and CaF_2. Further, we will demonstrate that a neglect of multiphonon processes in the analysis of the PDF as was done in Ref. 1 will give rise to serious errors.

II. COMPUTER SIMULATIONS

The PDF $\rho(r)$ may be computed either directly in real space or by Fourier transforming results obtained in reciprocal space. Each approach has its pros and cons for a comparison with an experimental PDF. A calculation in reciprocal space has the advantage that it is closely related to the analysis of a neutron powder experiment. Hence, it is relatively straightforward to consider the influence of experimental parameters such as the resolution and the accessible Q range. On the other hand, it is virtually impossible to include the multiphonon contribution to $\rho(r)$ in the calculation, so that $\rho(r)$ can be calculated only in the one-phonon approximation.

A calculation in real space automatically includes the multiphonon contribution to $\rho(r)$ and therefore appears to us as the better choice. It is computationally demanding but not impossible to take the finite experimental resolution and the finite Q range into account as well. To do this, $\rho(r)$ calculated in real space has to be Fourier transformed into reciprocal space, corrected for experimental effects, and then backtransformed into real space.

Dimitrov *et al.*[1] have opted for the reciprocal space approach. We have used the same approach in Sec. II A for a systematic study of the sensitivity of the PDF to details of the phonon spectrum. We think that the neglect of the multiphonon contribution is not serious for an intercomparison of $\rho(r)$ calculated from various lattice dynamical models. However, additional calculations using the real space approach show that the neglect of the multiphonon contribution is rather serious for a comparison of a calculated $\rho(r)$ with an experimental $\rho(r)$. This will be discussed in Sec. II B.

A. Reciprocal space approach

In a neutron powder experiment, the PDF $\rho(r)$ is obtained from the neutron scattering law $S(Q)$ via Fourier transform:

$$\rho(r)=\frac{G(r)}{4\pi r^2}=\rho_0+\frac{1}{2\pi^2 r}\int_0^\infty dQ[S(|\mathbf{Q}|)-1]Q\sin(Qr), \tag{1}$$

where $G(r)$ denotes the more common definition of the PDF so that for monoatomic crystals the integrals over the peaks of $G(r)$ give the number of atoms in the coordination sphere. $S(Q)$ can be decomposed into $S(Q)=S_0(Q)+S_1(Q)+S_n(Q)$ where S_0, S_1, and S_n denote the elastic part, the one-phonon part, and the multiphonon part of the scattering law, respectively. Following the procedure of Ref. 1, $S_n(Q)$ was neglected in our simulations, whereas $S_0(Q)$ and $S_1(Q)$ were computed from the structure and a specific lattice dynamical model. As mentioned above, the neglect of $S_n(Q)$ is not serious for an intercomparison of $\rho(r)$ calculated from various lattice dynamical models as the multiphonon terms are less sensitive with respect to details in the phonon dispersion curves than the one-phonon part. The phonons influence S_0 via the thermal parameters U which were calculated using standard formulas.[2] The Fourier transform of S_0 was done by computing a Fourier sum instead of a Fourier integral in order to avoid noise from a finite mesh size in Q. The calculation of $S_1(Q)$ is in principle also straightforward but it requires a considerable computational effort: the single-crystal one-phonon cross section is calculated in a large sphere in Q space with $Q \leqslant Q_{max}$ and sampled into a two-dimensional field $S_1(Q,\omega)$ generally called the polycrystalline one-phonon scattering law. $S_1(Q,\omega)$ is then integrated over all energies to obtain $S_1(Q)$. Here Q_{max} has to be chosen sufficiently large to keep truncation errors in the Fourier transform below acceptable levels. Empirically, we found that the Debye-Waller factor e^{-2W} for $Q>Q_{max}$ has to be less than 0.1%. This implies that Q_{max} strongly depends on the thermal parameters of the material and for this reason on the temperature. The values of Q_{max} chosen in our calculations are summarized in Table I. The PDF calculated in the one-phonon approximation will be denoted $\rho_{01}(r)$. All the calculations were done for room temperature to allow a comparison with the study of Ref. 1. For each material, we compare the results for models of different complexity. The models labeled M1 are the most elaborate ones designed to describe the phonon dispersion curves published in the literature with good accuracy, i.e., with deviations between experimental and calculated frequencies of the order of 1% or less. These models are considered as reference models, and so any deficiencies of these models in describing the experimental data are irrelevant in the context of this study. All further models considered in this study were much simpler than M1. They were primarily designed with a view to obtain thermal parameters identical to those of M1. Further fine-tuning of the parameters may lead to an even better reproduction of the PDF and was sometimes attempted by trial and error, but not by a real fit. We note that a fit of the model parameters to the PDF would be computationally extremely demanding and that already for models with only two parameters.

TABLE I. Thermal parameters U and range of Q for the Fourier transform.

Element	$U(296\ \mathrm{K})$ [Å^2]	Q_{max} [1/Å]	$U\cdot Q_{max}^2$
Ni	0.00476	44	9.2
Rh	0.00301	50	7.5
Nb	0.00672	44	13.0
CaF$_2$: Ca/F	0.00638/0.00885	34	7.4/10.2

The PDF of Ni and its decomposition into the contribution from the elastic and one-phonon parts of the neutron spectrum is shown in the upper panel of Fig. 1. A close inspection of the curve labeled ρ_{01} reveals that there is a slight undershoot at both sides of the first peak which is due to the neglect of multiphonon terms. This demonstrates that in the one-phonon approximation the peaks in the PDF are no longer Gaussian-like. Except in the wings, however, the peaks can be rather well fitted by a Gaussian profile which we have used to extract information on the width throughout this paper. We note that the one-phonon contribution does not change the area under the peaks but leads to a narrowing of the peaks which reflects the correlation between the displacements of near neighbors. On these grounds, it is understandable that the narrowing is most pronounced for the nearest-neighbor peak and gradually vanishes with increasing distance. It is precisely the amount of this narrowing and its distance dependence which is all the basis for any attempt to determine details of the phonon spectrum from such data other than the summary information contained in the thermal parameter. In the case of Ni at room temperature, the narrowing is of the order of 10% for the first peaks up to $r<5$ Å (Table II). Values calculated for a sample temperature of $T=10$ K are included in Table II to show that the narrowing of the PDF peaks is strongly reduced at low temperatures and drops off very rapidly with increasing distance. This is a consequence of the Bose factor in the one-phonon cross section which is $\sim 1/\omega$ at $T=0$ and approaches $\sim 1/\omega^2$ at high temperatures. Therefore, at high temperatures the PDF mainly probes the low-frequency part of the phonon spectrum where the phonon dispersion curves are nearly linear.

For any attempt to get reliable phonon information from powder diffraction it is decisive to know how much the narrowing of the PDF peaks associated with the phonons depends on the parameters describing the interatomic interactions. To this end, the PDF calculated from M1 is compared to that calculated from an extremely simple one (M2) containing just one longitudinal nearest-neighbor force constant adapted to yield the same thermal parameter. The difference curve PDF(M1) − PDF(M2) shown in Fig. 1 reveals that the

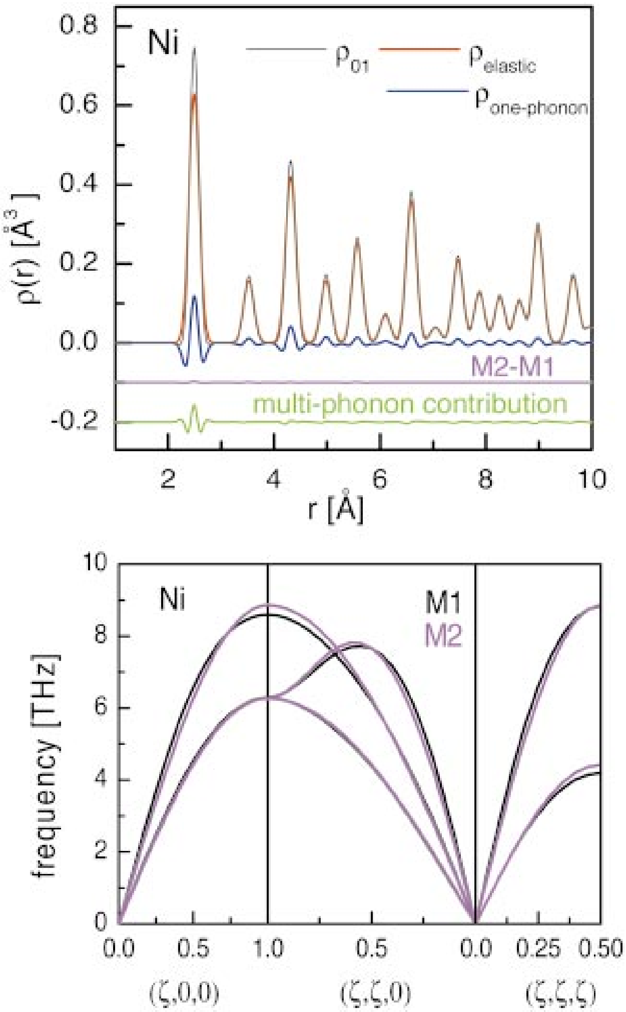

FIG. 1. (Color) Top: the PDF $\rho_{01}(r)$ of Ni as calculated from model M1 and its decomposition into the elastic and the one-phonon contribution of $S(Q)$. Further shown are the difference in $\rho(r)$ when going from model M1 to model M2 and the multiphonon contribution to $\rho(r)$ for model M1. Bottom: phonon dispersion curves of Ni as calculated from model M1 and from model M2. We note that model M1 closely reproduces the experimental data of Ref. 3.

TABLE II. Widths of peaks in the PDF of Ni below 9 Å in units of the asymptotic value calculated from the thermal parameter. The left-hand values were obtained from Gaussian fits to the peaks calculated in the one-phonon approximation, the right-hand ones calculated from Eq. (2).

r[Å]	M1 (296 K)	M2 (296 K)	M1 (10 K)
2.492	0.847/0.790	0.844/0.786	0.927/0.914
3.524	0.930/0.922	0.924/0.915	0.986/0.985
4.316	0.910/0.895	0.908/0.893	0.975/0.973
4.984	0.910/0.895	0.910/0.896	0.973/0.972
5.572	0.946/0.941	0.942/0.937	0.991/0.990
6.593	0.937/0.930	0.936/0.930	0.987/0.987
7.475	0.952/0.955	0.950/0.952	0.993/0.994
7.880	0.953/0.952	0.952/0.950	0.994/0.993
8.984	0.958/0.958	0.957/0.954	0.994/0.994

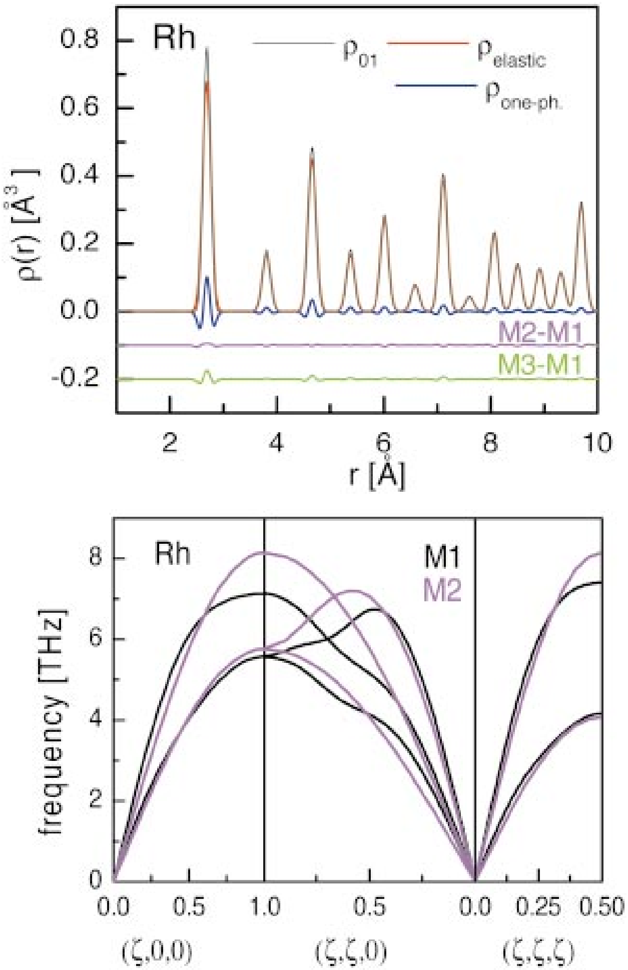

FIG. 2. (Color) Top: the PDF $\rho_{01}(r)$ of Rh as calculated from model M1 and its decomposition into the elastic and the one-phonon contribution of $S(Q)$. Further shown are the difference in $\rho(r)$ when going from model M1 to model M2 or to model M3. Model M3 differs from model M2 by a general increase of phonon frequencies by 3%. The thermal parameters calculated from model M1 and from model M3 are identical. Bottom: phonon dispersion curves of Rh as calculated from model M1 and from model M2. Model M1 reproduces the experimental data of Ref. 4 very closely.

difference between the two PDF's is extremely small. A look on the dispersion curves calculated from the two models, however, makes it quite understandable that the PDF is barely affected by the sophistications of model 1 containing 16 parameters for interactions extending up to the fifth nearest neighbors: The lower part of Fig. 1 reveals that the phonon curves of Ni can be quite satisfactorily described by the very simple model. Therefore, Ni appears as an unsuitable candidate for a search of signatures of a multiparameter model from the very beginning. It was chosen here as an example mainly because the authors of Ref. 1 claimed to have extracted nine model parameters from neutron powder diffraction data.

Rhodium is a fcc metal where long-range forces are indispensable to arrive at a satisfacory description of the phonon dispersion curves.[4] Nevertheless, a very crude model (labeled M2), containing just one adjustable parameter—

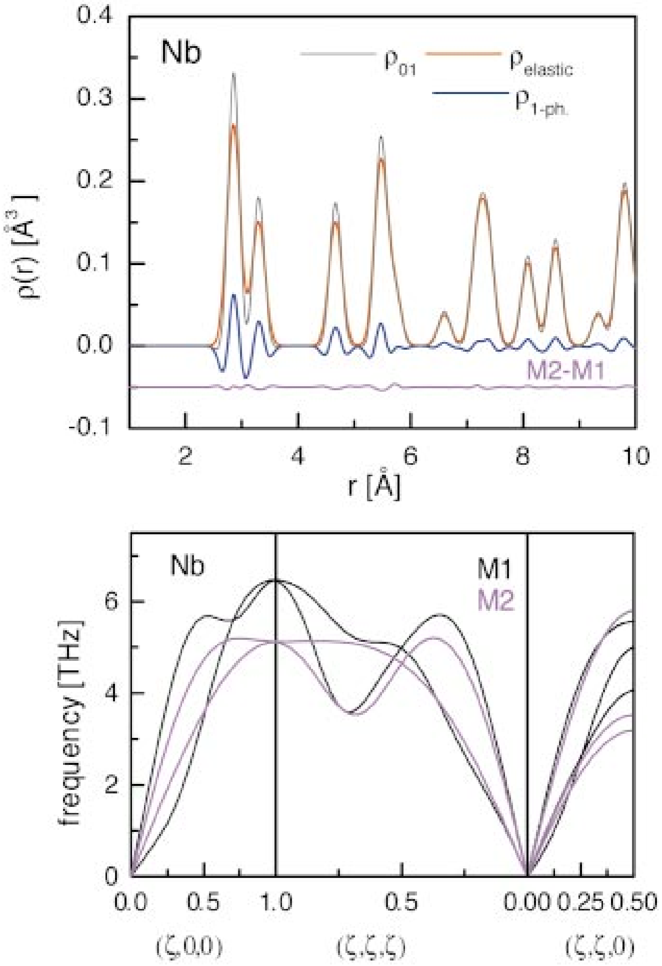

FIG. 3. (Color) Top: the PDF $\rho_{01}(r)$ of Nb as calculated from model M1 and its decomposition into the elastic and the one-phonon contribution of $S(Q)$. Further shown are the difference in $\rho(r)$ when going from model M1 to model M2. Bottom: phonon dispersion curves of Nb as calculated from model M1 and from model M2. Model M1 reproduces the experimental data of Ref. 5 very closely.

chosen to provide the best reproduction of the reference PDF—yields a very satisfactory description of the PDF (see Fig. 2). The differences between the PDF calculated from the simple and the elaborated model M1, respectively, are certainly smaller than those presented in Ref. 1 as differences between the experimental PDF and the theoretical PDF calculated from their best model for Ni. This means that it cannot be hoped to discriminate between a very good model like M1 and a model as crude as M2 on the basis of neutron powder diffraction data alone. We note that the sensitivity of the PDF analysis increases somewhat if the models are constrained to yield the correct thermal parameters. For example, retuning the single parameter of M2 in order to reproduce the thermal parameter of M1 leads to a PDF with somewhat larger differences with respect to that of M1 (shown in Fig. 2 as a difference curve M3 − M1). This retuning leads to a very moderate increase of the phonon frequencies of about 3%. The lesson from this finding is the following: the PDF is rather sensitive to changes of the thermal parameter, but not to the shape of the phonon dispersion curves. Therefore, adjustment of the model parameters producing slight changes of the thermal parameters can largely mimic pecularities in the PDF associated in reality with special features in the phonon dispersion curves. In order to avoid this pitfall, it would be necessary to have precise values for the thermal parameters available obtained by some other technique, i.e., by a Rietveld analysis of the data prior to PDF analysis. However, such an analysis has to provide thermal parameters with a precision of about 1% to be of real help.

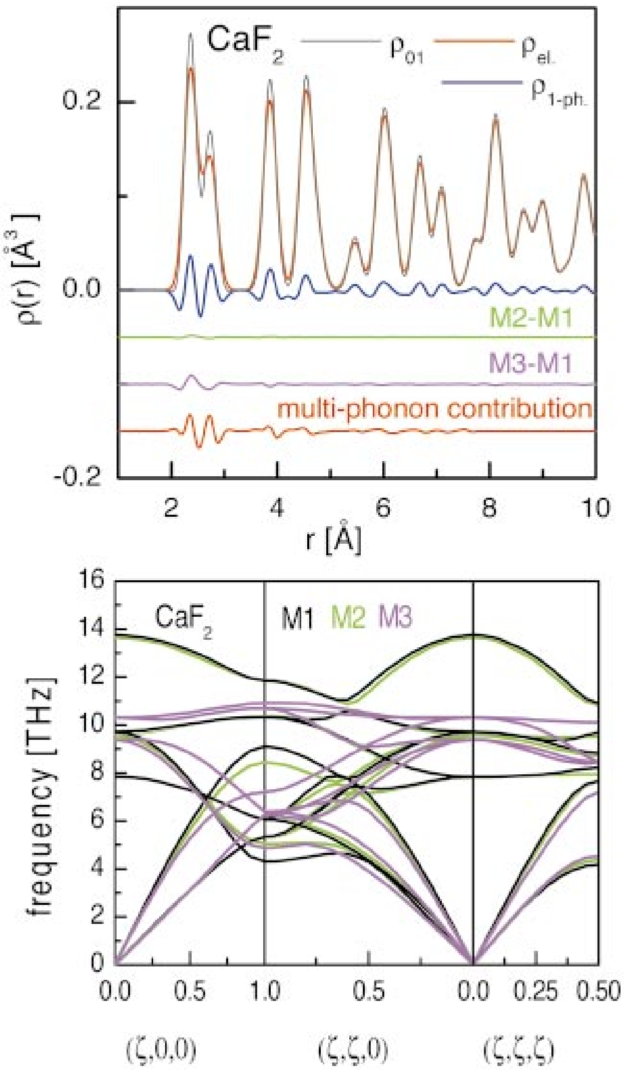

FIG. 4. (Color) Top: the PDF $\rho_{01}(r)$ of CaF_2 as calculated from model M1 and its decomposition into the elastic and the one-phonon contribution of $S(Q)$. Further shown are the difference in $\rho(r)$ when going from model M1 to model M2 or to model M3 and the multiphonon contribution to $\rho(r)$. Bottom: phonon dispersion curves of CaF_2 as calculated from model M1, M2, and M3. Model M1 closely reproduces the experimental data of Ref. 6.

Niobium is a bcc metal whose phonon dispersion curves exhibit very pronounced anomalies,[5] e.g., an upward curvature of transverse acoustic branches in the (1,0,0) and (1,1,1) directions (see the curves labeled M1 in Fig. 3, lower panel). Long-range forces up to the eighth neighbor are necessary to arrive at a satisfactory description of the phonon anomalies. The slopes of the transverse acoustic branches are quite low which leads to a rather large thermal parameter. On the other hand, the longitudinal nearest-neighbor force constant is fairly large as is evidenced by the rather steep slope of the longitudinal acoustic branches. As a consequence, the inelastic contribution to the PDF leads to a much stronger narrowing of the peaks calculated from the elastic contribution than in Ni or Rh. So Nb appears as a good testing ground for the sensitivity of the PDF to the details of the phonon spectrum because of both the presence of pronounced phonon anomalies and the relatively strong inelastic contribution to the PDF. Nevertheless, a very crude model missing all the anomalous features (M2) reproduces the PDF very closely (see Fig. 3). The reproduction of the PDF might further be improved by adjusting the four parameters of the model by a real fit procedure, whereas the present choice was obtained by trial and error. We note that such a fit would barely, if at all, improve the agreement between the dispersion curves of M1 and M2, because the force constants of M2 do not extend beyond second-nearest neighbors.

As a last example, we took CaF_2 which is a cubic compound with three atoms in the unit cell and hence nine phonon branches in each direction. In view of the low sensitivity of the PDF to details of the phonon spectrum already for monoatomic solids with only one atom per unit cell, an attempt to extract dynamics from powder diffraction for a more complex solid appears daring from the very beginning. We investigated CaF_2 nevertheless because it was claimed by the authors of Ref. 1 that their procedure works for this compound as well. The phonon curves fitted to the experimental data published in the literature[6] on the basis of a shell model (labeled M1) similar to that employed in Ref. 1 containing 12 parameters are shown as black lines in Fig. 4. When the model is strongly simplified to a rigid ion model with only four adjustable parameters (M2) the overall description of the dispersion curves remains quite satisfactory (see the green lines in Fig. 4). For this reason, it is quite understandable that the PDF is barely affected by the deficiencies of M2, and it will be certainly impossible to decide from powder diffraction data alone that M2 is definitely poorer than M1. Here M2, being already very simple, one has to go to unphysical models to arrive at a PDF which is significantly different from that given by M1. As such a model, we have chosen a force constant model without any Coulomb forces (M3) which for this reason cannot reproduce the LO-TO splitting observed in an ionic insulator like CaF_2. Consequently, the description of the optic branches by such a model is very poor (Fig. 4). In spite of the severe deficiencies of M3, the PDF does not differ from the PDF of M1 to a great extent. Certainly, the wiggles appearing in the difference curve M3-M1 at $Q \ll 2.5$ Å are relatively large so that it might be possible to rule out M3 on the basis of very accurate powder diffraction data. The experiments reported in Ref. 1, however, appear not to have achieved the necessary accuracy to rule out a model like M3 as is evident from the size of the deviations between ρ_{expt} and ρ_{theor} (see Fig. 3 in Ref. 1).

B. Real space approach

So far, we have calculated the PDF from $S(Q)$ via Fourier transform. Recently, Chung and Thorpe[7] proposed a different approach to study phonon effects in the PDF using displacement correlation functions. In the harmonic approximation, the PDF consists of a series of Gaussian peaks from each pair in the system centered at R_{ik} with width σ_{ik} given by

$$\sigma_{ik}^2=\frac{\hbar}{2N}\sum_{\mathbf{q},s}\frac{2\langle N_{\mathbf{q},s}\rangle+1}{\omega_s(\mathbf{q})}\left|[\mathbf{u}_{lk}(\mathbf{q},s)-\mathbf{u}_{0i}(\mathbf{q},s)]\mathbf{R}_{ik}\right|^2/R_{ik}^2, \tag{2}$$

where the displacements $\mathbf{u}_{lk}$ are given by

$$\mathbf{u}_{lk}=\mathbf{e}_k(\mathbf{q},s)\exp[i\mathbf{q}\cdot\mathbf{R}(l,k)]\sqrt{M_k}. \tag{3}$$

Here, $\mathbf{R}(l,k)$ is the position vector of the kth site in the lth unit cell associated with an atom of mass M_k and $\mathbf{R}_{ik}=\mathbf{R}(l,k)-\mathbf{R}(0,i)$ denotes the distance vector between two sites in the lattice. $\langle N_{\mathbf{q},s}\rangle$ is the Bose occupation number and $\omega(\mathbf{q},s)$ and $\mathbf{e}_k(\mathbf{q},s)$ are the eigenvalues and the eigenvectors of the dynamical matrix. The summation runs over N wave vectors $\mathbf{q}$ and $3n$ phonon branches in the Brillouin zone where n is the number of atoms in the unit cell.

When the mixed product in the quadratic form of Eq. (2) is omitted we arrive at the familiar result of a width obtained from a convolution of two Gaussians whose widths are given by the thermal parameters of the atomic species with labels i and k. The mixed product accounts for the narrowing of the peaks associated with the fact that the atomic motions are correlated with each other to some degree, in particular for the next-nearest neigbors. It tends to zero for large interatomic distances.

It has been argued by Dimitrov *et al.*[9] that the above formalism neglects higher-order effects arising from the powder average. These effects which are of the order of $(U_i+U_k)/R_{ik}^2$ (U_i thermal parameter of atomic species i) lead to peak shifts and non-Gaussian peak shapes in highly anisotropic crystals. Calculations based on the treatment of the powder average as given in Ref. 9 revealed that for all cases discussed in this article (cubic lattices with all sites having either cubic or tetrahedral environment and thermal parameters of moderate size), Eq. (2) provides an excellent approximation. We find that the first neighbor peak is very well described by a Gaussian profile with a width that differs by less than 0.1% from that calculated by Eq. (2). Peak shifts lie between 0.13% and 0.24%. At larger distances differences are even smaller.

The calculations using the real space formalism are not only in general much faster and more transparent than those using the method in reciprocal space but, most importantly, include all higher-order phonon terms. This allows us to extract the so-far-neglected multiphonon contribution to the PDF by comparing the results of the two approaches. Results for Ni on the basis of model M1 using expression (2) are listed in Table II and a difference curve is shown in the bottom part of Fig. 1 (top). Apparently, the multiphonon contribution to the PDF is by no means negligible. In particular, the width of the first peak in the PDF is significantly

TABLE III. Narrowing of the first-neighbor peak in Ge at various temperatures calculated in the one-phonon approximation and from Eq. (2).

T [K]	$U(296\ \mathrm{K})$ [Å^2]	$\sigma/\sqrt{U}$ (one-phonon)	$\sigma/\sqrt{U}$ [Eq. (2)]
296	0.00712	0.746	0.481
100	0.00281	0.769	0.580
10	0.00164	0.827	0.738

reduced, whereas the influence of the multiphonon contributions decreases rapidly with increasing distance *r*. In the case of Ni, the width of the first peak is reduced by 7% and the peak height is increased accordingly. As can be seen from Fig. 4, the multiphonon contributions to the PDF are quite important in CaF_2 as well. We note that the multiphonon effects are larger than the differences between the various models that we have discussed in this article. Hence, it follows that a calculation based on the one-phonon contribution only is inadequate for a comparison with experiment when it is aimed at deducing details of the lattice vibrations from an experimental PDF. In light of these results, it is surprising that for Ni Dimitrov *et al.*[1] achieved a nearly perfect agreement between experiment and theory in spite of their neglect of higher-order terms. As the phonon dispersion curves of Ni have been determined experimentally with high precision and as the dispersion curves are very well reproduced by the model used, the PDF of Ni can be predicted with high accuracy. Therefore, we think that the solution of this puzzle has to be sought in flaws of the experimental technique: damping needed to reduce truncation effects in the Fourier transform due to an unsufficient Q range will broaden the peaks, whereby the effect will be particularly large for the first peak in the PDF. Presumably, these broadening effects lead to the wrong impression that the influence of the phonons can be well accounted for by considering one-phonon contributions only.

In this context, we would like to point out that the narrowing of the first peak due to correlation effects is not always as moderate as in those materials treated above. For instance, it is considerably more pronounced in covalent materials of the diamond or zinc blende structure which are characterized by strong bond stretching but weak bond bending forces. This has been demonstrated in Ref. 7 for InAs where the width of the first neighbor peak is reduced by more than 50% at $T = 300$ K. Our own calculations have shown that the one-phonon contribution accounts only for half of the total effect. Further, we have found that the influence of the multiphonon contributions cannot be neglected even at low temperatures. Some exemplary results for Ge are listed in Table III. We note that a similar situation is found in perovskite-related structures. In these materials, some thermal parameters are quite large due to soft phonons associated with rotations of octahedra. On the other hand, the bonds within the octahedra are quite stiff, and therefore correlation effects are large.

At first sight, the strong influence of the multiphonon processes on the width of the first peak in the PDF may seem astonishing. However, one has to recall that at large Q the scattering function $S(Q)$ is dominated by multiphonon processes. We found that the multiphonon cross section fluctuates around the asymptotic limit approximately sinusoidally with a period that is determined by the distance between nearest neighbors. This correlates with the observation that the influence of the multiphonon contributions is essentially confined to the first peak in the PDF.

III. CONCLUSIONS

In the analysis of an experimental PDF, we have to consider three levels of sophistication.

(i) Elastic approximation: here, the width of the peaks in the PDF is solely determined by the thermal parameters. On these grounds, it is impossible to gain more information from the data than could be obtained from a Rietveld analysis. What is worse, the analysis will invariably yield too small thermal parameters because the peaks in the PDF are sharper than expected from the thermal parameters because of correlation effects. Using a large range in *r* for the determination of the thermal parameters will reduce the error associated with the neglect of correlation effects. However, the useful range in *r* is mostly very limited because of the large number of overlapping peaks already at moderate *r*. For instance, the extensively studied compound La_2CuO_4 has no less than 169 peaks in the PDF in the range $r < 8$ Å. For these reasons, we question the claim of Billinge[8] that a PDF analysis is superior to a Rietveld analysis with respect to the accuracy of the thermal parameters—at least when phonon effects are not even considered in the one-phonon approximation.

(ii) One-phonon approximation: the narrowing of the peaks in the PDF is taken into account as discussed in Sec. II A. This will lead to a quite accurate description of the peak widths except for the first peak whose width will remain significantly overestimated. Rather crude lattice dynamical models are sufficient to reproduce the narrowing associated with the correlated motions of the atoms. Consequently, they are sufficient to extract precise values of the thermal parameters when the first peak is left out in the evaluation. On the other hand, this also means that very little can be learned about details of the phonon spectrum from such an analysis. It is true that the sensitivity of the PDF to the dynamics increases with increasing thermal parameters so that phonon effects in the PDF may become quite strong, in particular for the first peak. Unfortunately, the importance of multiphonon effects increases accordingly. Based on these findings, we strongly question the claim of Dimitrov *et al.*[1] to have *successfully* implemented a procedure to extract phonon information from neutron powder diffraction.

(iii) Real space calculation: all the peak widths can be predicted with high accuracy, including the width of the first peak. Consequently, thermal parameters can be obtained very reliably. A further argument in favor of a real space calculation is the fact that it is computationally less demanding than the calculation in reciprocal space in the one-phonon approximation if one is interested only in a restricted range of *r* where correlation effects are important. A real space calculation is certainly the proper starting point for any attempt to deduce details of the phonon spectrum from an experimental PDF, because the neglect of multiphonon contributions entails errors in the theoretical PDF which are larger than those resulting from pronounced differences in the phonon dispersion curves.

In conclusion, even within a proper framework for the analysis we see little perspective for attempts to deduce details of the phonon dispersion curves from an experimental PDF—the PDF is just too insensitive to such details. Finally, we would like to point out that the insensitivity of the PDF to details of the phonon dispersion curves is all too plausible: to begin with, the inelastic contributions to the PDF are only a small fraction of the total PDF. Further, the inelastic contributions are averaged over all directions and over all phonon energies. Moreover, there are very few if any nonoverlapping peaks in the PDF so that the useful range in r is very small—a meager basis to extract phonon information from neutron powder diffraction. On the other hand, we emphasize that correlation effects should be accounted for—at least in an approximate manner—if one aims to extract structural details such as local distortions from the first peaks of an experimental PDF.

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[1] D.A. Dimitrov, D. Louca, and H. Röder, Phys. Rev. B **69**, 6204 (1999).

[2] W. Marshal and S.W. Lovesey, *Theory of Thermal Neutron Scattering* (Oxford University Press, Oxford, 1971), p. 73.

[3] G.A. DeWit and B. Brockhouse, J. Appl. Phys. **39**, 451 (1968).

[4] A. Eichler, K.-P. Bohnen, W. Reichardt, and J. Hafner, Phys. Rev. B **57**, 324 (1998).

[5] B.M. Powell, P. Martel, and A.D.B. Woods, Phys. Rev. **171**, 727 (1968).

[6] M.M. Elcombe and A.W. Pryor, J. Phys. C **3**, 492 (1970).

[7] J.S. Chung and M.F. Thorpe, Phys. Rev. B **55**, 1545 (1997).

[8] S. J. L. Billinge, in *Local Structure from Diffraction*, edited S.J.L. Billinge and M.F. Thorpe (Plenum, New York, 1998), p. 137.

[9] D.A. Dimitrov, H. Röder, and A.R. Bishop, cond-mat/0009160 (unpublished).