

## Lattice dynamics of CuCl

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A satisfactory fit for CuCl phonon dispersion relations is obtained for the first time. This fit is achieved by modifying the branch assignment of a few  $\Sigma$  phonons and by applying a double-shell model to fit the observed phonon data.

The lattice dynamics and related properties of CuCl have recently been of considerable interest mainly in experimental researches, that included Raman scattering,<sup>1-3</sup> measurement of elastic properties,<sup>4-5</sup> and inelastic coherent scattering of neutrons.<sup>6</sup> The reason for this interest is that although CuCl is structurally simple (it has a zinc-blende structure), its physical properties are quite peculiar. It is very anharmonic,<sup>5</sup> its phonon structure is considerably more complex than the phonon spectra of<sup>7</sup> CuBr and<sup>8</sup> CuI, its Raman spectrum shows some peculiarities,<sup>2,3</sup> and it has a large negative thermal-expansion coefficient<sup>9</sup> in the temperature range of 0 to 100 °K.

In the present article we are mainly concerned with the lattice dynamics of CuCl. CuCl is considered to be more ionic than CuBr and CuI, and in fact, it is the most ionic of all zinc-blende crystals, according to the Phillips criterion<sup>10</sup> of ionicity. It happens to be just outside the range allowed for the onset of NaCl structure.<sup>11</sup> Martin<sup>12</sup> suggests that this fact is intimately related to the unusual elastic properties of CuCl. The phonon spectrum of CuCl also shows a few peculiarities.<sup>6</sup> For example, the TA branches are unusually flat along all high-symmetry directions, and there are crossings of TO and LO modes. The most noticeable peculiarity is in the LA branch of the [110] direction ( $\Sigma$ ), where a large and unusual maximum appears to be in the middle of the branch. It is therefore not surprising that attempts to fit the observed phonon dispersion relations to simple models were not successful.<sup>6</sup> In contrast, the phonon spectra of CuBr and CuI were much smoother, and no special difficulty was encountered in fitting the dispersion relations to rigid-ion models.<sup>7,8</sup>

In tackling the lattice dynamics of CuCl we noticed that Carabatos *et al.*<sup>6</sup> applied a rigid-ion model as well as a fully deformable ion model. Both these models failed to reproduce the main features of the phonon spectrum, and even predicted unstable modes for some TA branches. In attempting to find a more satisfactory model, we tried several preliminary models. One of these (Model A) is shown in Fig. 1, and it consists of

a seven-parameter shell model<sup>13</sup> that was obtained from a best fit to all the phonon data. Model A already shows some improvements over earlier attempts,<sup>6</sup> mainly in eliminating unstable modes, but we still regard it as unsatisfactory in fitting the data. Moreover, it was found that Model A was very sensitive to the particular values of its parameters and lost its stability for small changes in them. In particular, the closeness in energy of the two TA modes of the  $\Sigma$  direction was responsible for this sensitivity. In attempting to improve over Model A we tried various ideas. At first we tried to include all the second nearest neighbors in the repulsive part of the dynamical matrix with as many as possible disposable parameters. In order to invoke more Fourier components, we even tried to include third and fourth nearest neighbors, but all this had very little effect on the fit.

We were somewhat more successful in trying a "breathing" shell model<sup>14</sup> (BSM). The BSM allows for a change in the volume (breathing) of the Cl electronic shell. The effect of the BSM is most pronounced at those wave vectors  $\vec{q}$  for which

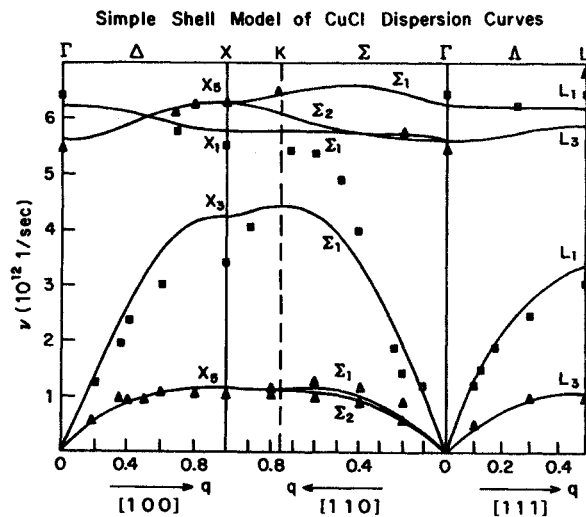


FIG. 1. Best fit results of a simple shell model (Model A) for the phonon spectrum of CuCl. The experimental results are taken from Carabatos *et al.* (Ref. 6).

the Cl ions are almost motionless, since for this condition they have a sufficiently large space around them to allow for breathing. Indeed, the main improvement due to the BSM was at  $X$  and  $L$  points, but the BSM was still inadequate in fitting the data in other directions, in particular, the LA ( $\Sigma$ ) maximum. The BSM also showed high sensitivity to the exact values of its parameters, and tended to lose its stability for small changes in them.

In all our preliminary attempts mentioned so far it was taken for granted that the phonons observed at the apparent maximum along the  $\Sigma$  direction were LA phonons. In particular we refer to a group of three phonons observed in the range of  $0.5 < q < 0.7$  and in the energy range 5.0–5.5 THz. Now there exists also an LO mode that belongs to the same irreducible representation  $\Sigma_1$  as does the LA mode. Moreover, it may be possible that these two modes are also close in energy and therefore could be indistinguishable from each other under the existing experimental conditions.<sup>15</sup> As a result of this it is no longer self-evident that the LA assignment is the only valid one for these phonons. Having made this observation, we repeated the calculations under the assumption that this group of phonons be given an LO assignment. This assumption removes some of the peculiarity of the CuCl phonon spectrum, and brings it more into accord with CuBr and CuI. We recognize that this interpretation of the experimental data needs more support by observation, but at present it is fully compatible with existing data, including elastic constants. It should be pointed out, however, that the experimental data near the “problematic” range are very scant, and additional measurements are greatly needed to clarify this point.

While this assumption had very little effect on the simple shell model (Model A), its success with the BSM was quite striking. It removed all instabilities from the TA branches, it separated the two TA ( $\Sigma$ ) modes, much more in accord with experiment, and accentuated the flatness of the TA branches in all high-symmetry directions.

However, the over-all fit, although improved, was still inadequate, especially near the “problematic” group of phonons. This model is termed Model B; it contains eight adjustable parameters that are listed in Table I.

In a recent publication Weber<sup>16</sup> introduced a new version of the shell model which he calls “double-shell model” (DSM). The motivation for the DSM was the explanation of the strong anomalies observed in the phonon dispersion relations of some of the transition metal carbides, in particular<sup>17</sup> TaC and<sup>18</sup> NbC. For this purpose Weber assumed an additional  $d$ -electron shell coupled to the ionic core which interacts with neighboring  $d$  shells. In the case of the transition metal carbides this contribution can cause a resonance-like behavior in part of the dynamical matrix elements for special  $\vec{q}$  vectors, and this brings about the phonon anomalies at these wave vectors.

Having exhausted all the possibilities with existing models we looked for new ideas having better potentialities for treating the phonon spectrum of CuCl. In doing so we became aware that the main source of difficulty might be the Cu electronic  $d$  shell. The performance of the DSM in fitting the phonon anomalies of TaC and NbC made it an attractive candidate for our venture, all the more so since, unlike in the transition metal carbides, all that was expected here was just an improvement in fitting the experimental data that did not show any strong anomalies. On the other hand, the physical situation of CuCl is very different from that of TaC and NbC, so that it is not easy to see why the DSM would be justifiable for use here.

In the case of CuCl the Cu<sup>+</sup> ions have a complete  $d$  shell and no outer electrons. In the solid the situation is considerably modified, and it is possible to get some insight from the electronic band structure of the solid. Actually, the band structure of CuCl was recently calculated,<sup>19</sup> and its valence bands have the following properties: (a) they are fairly flat throughout the zone and form two groups of bands, separated by approximately 3 eV; (b) The valence bands have largely Cu  $d$ -like character. These findings are also supported by optical

TABLE I. The parameters of models  $A$ ,  $B$ , and  $C$  are given in units of  $e^2/2v_0$ , where  $v_0$  is the volume of a unit cell. The parameters  $z$ ,  $y$ ,  $K$ ,  $A$ ,  $A'$ ,  $A''$ , and  $B$  are customary to shell models and follow Ref. 13.  $G$  is the “breathing” parameter (Ref. 14),  $A_D$  and  $K_D$  the double-shell parameters and they are explained in the text.

Model	$z$	$y$ (Cl)	$K$ (Cl)	$A$	$B$	$A'$ (Cl)	$A''$ (Cu)	$G$	$A_D$	$K_D$
$A$	0.55	-1.51	16.14	9.55	9.45	-1.67	0.8	...	...	...
$B$	0.45	-1.53	17.23	9.36	8.81	-1.85	0.95	158	...	...
$C$	0.64	-1.42	15.48	9.14	9.64	-1.97	2.62	...	-0.95	6.35

absorption data.<sup>19</sup>

These results are very helpful for our purpose, since they mean roughly that the Cu *d*-shell is split into two subshells with a large energy gap in between. This by itself can be regarded as a justification for the use of the DSM for CuCl, so that different springs are attached to each subshell.

The details of the DSM are given in Ref. 16.

The inclusion of another shell labeled *D* adds two disposable parameters  $K_D$  and  $A_D$ , which represent Cu core-*d*-shell interaction *a* and *d*-shell-*d*-shell interaction between two Cu ions, so that our DSM is the simplest possible and has altogether nine parameters. We did not include interactions between Cu shells and Cl shells because we believe that these are absorbed in the Cu-Cl repulsive matrix. The best fit calculations for the DSM gave the best results, and they are presented in Fig. 2. The fit of the DSM results to the CuCl phonon dispersion relations is very good, and there are almost no significant departures of experimental observations from model predictions. The DSM model is termed here Model C, and we bring the numerical values of its parameters in Table I. It is interesting to note that although we change the assignment for a group of phonons in the  $\Sigma$  direction, we still have a maximum in the LA branch in this direction. It is also important to mention that we also tried the DSM with the original phonon assignment, but it yielded poor results.

It may be argued, that the DSM increases the number of adjustable parameters, and this in itself may explain the success in fitting the data. The answer to this is that not every increase in the number of parameters is necessarily helpful in fitting the data. For example, in our preliminary attempts we employed models with as many as 13 parameters with very little effect. Moreover, even the DSM did not help except when we changed the assignment of a few phonons. The meaning of all this is that the performance of the DSM in fitting the phonon data of CuCl is by no means self-evident.

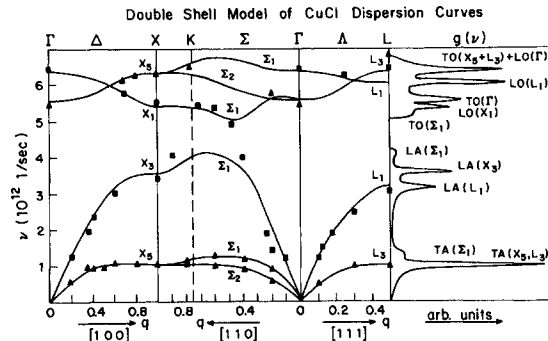


FIG. 2. Best fit results of a double-shell model (Model C) for the phonon spectrum of CuCl. The experimental points are taken from Carabatos *et al.* (Ref. 6).  $g(\nu)$  based on this model is also shown.

Model C is used for the calculation of the phonon density of states  $g(\nu)$  of CuCl, and it is shown also in Fig. 2. The calculation was performed by the extrapolation method.<sup>20</sup> In view of the considerable anharmonicity of CuCl it is dubious if this  $g(\nu)$  can serve for the purpose of calculating thermodynamical properties. It is interesting, however, to observe that there are two gaps in  $g(\nu)$ . One is between the optic and acoustic modes and it is in the frequency range 4.5–5.0 THz. The second one is a quasigap in the range 1.5–2.5 THz and it originates from the energy difference between the low-energy TA modes and the much higher LA modes.

In conclusion, in the present article we bring for the first time a successful model representation of the phonon spectrum of CuCl. The calculation is based on a certain modification in the assignment of a few phonons and then on a double shell model for the copper *d* shell. We believe that the success of the DSM in the case of CuCl is meaningful and has to do with the intrinsic interactions existing between Cu ions in CuCl.

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