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COHERENT POTENTIAL APPROXIMATION AND STRONGLY ANHARMONIC SYSTEMS: CRYSTALS OF PARA-HYDROGEN AND NEON RESP. HYDROGEN ATOMS

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Abstract.- For mixtures of p-hydrogen and neon in the solid state phonon calculations have been performed by combining the CPA and the self consistent phonon approximation (SCP) to include the strong anharmonicity of the system. The structure changes and the phonon spectrum have been calculated as function of the concentration. The method has also been applied to mixtures of p-H₂ and hydrogen atoms.

Under the solids which are known to be quantum crystals there are several systems of two or more kinds of molecules statistically mixed on the lattice positions, e.g. o-H₂, p-H₂ mixtures, H₂-D₂, H₂-Ne mixtures. These systems are strongly anharmonic because of changing force constants as function of the mean distance of the molecular pairs and of the large amplitudes of the zero-point motion. To calculate their phonon resp. roton spectra the theories of statistically disordered crystals which are harmonic have to be generalized to take into account strong anharmonicities.

The single site coherent potential approximation (CPA) is well known to be the best working method to calculate phonon spectra of disordered crystals abstracting from its weakness in describing pair and clustering effects. We have combined the CPA and the self-consistent phonon approximation (SCP) to get a first insight into the dynamics of anharmonic and disturbed crystals of two compounds.

One of the simplest disturbed systems seems to us to be the p-hydrogen neon system since the pair potentials are roughly equal and the mass ratio is 10 ("isotopical disorder"). The large mass ratio produces a big difference in the zero point motion. Therefore, the structure in the neighbourhood of one guest molecule in a host crystal is strongly change and with it the force constants. We have simplified the problem to a certain extent to reduce the numerical difficulties: the structure has been face centered cubic for all concentrations though high hydrogen concentrations are stable in the hexagonal closed packed structure. We have used always the regular cubic point symmetry for every lattice site occupied by a guest molecule. We have not considered
refined quantum effects (no quantum diffusion). This may turn out to be too much simplification: There may occur deviations from statistical mixing through correlations – static or time dependent. But the problem remains complicated enough and the numerical problems grow considerably with the model of the neighborhood of the guest molecule. We have started with a model where only the nearest neighbors could relax. This model turned out to be too rigid: the global lattice constant changed too much, the frequencies changed partly in a wrong direction. Therefore, we introduced another model with relaxations up to the fourth neighbor shell. All static and dynamic displacements were restricted not to violate the cubic symmetry.

Since hydrogen forms quantum crystals, the short range correlations have to be taken into account. We have done this with Jastrow factors of an appropriate kind.

The whole calculation turned out to be a voluminous one to be solved self consistently with several variational parameters: the lattice constant a, the static displacements from the lattice points of molecules in four shells in the neighborhood of a guest molecule $\Delta R_{ij}$ the width parameters $\gamma_{ij}$ of the displacement-displacement correlation function, and the parameters in the Jastrow factor. The iteration procedure turned out to be very difficult and special tricks had to be used to reach convergence. Calculations were performed mostly on the Ne-(p-H$_2$) system, a few on p-H$_2$-(Ne) and on p-H$_2$-(H atoms). The table contains the static structural changes, the figures show the spectra of the crystals, some Jastrow factors and the comparison of the mean lattice constant from which follows, that the model with relaxation of four shells is necessary to describe the local displacement field of the point defect formed by a guest molecule.

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<td>Ne+(p-H$_2$)$_0$</td>
<td>$5.2481$</td>
<td>$0.60$</td>
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<td>$\gamma_{ij}$</td>
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<tr>
<td>$\gamma_{ij}$</td>
<td>$4.4530$</td>
<td>$0.0064$</td>
<td>$---$</td>
<td>$---$</td>
<td>$6$</td>
</tr>
</tbody>
</table>

1) model with 4 relaxing neighbor shells
2) model with nearest neighbor relaxation only
3) $E(x) = \exp(-x^2/\gamma_{ij})$
4) $f(x) = \exp(-x^2/\gamma_{ij})+(1-a_x+\gamma_{ij})^2$ $a_x = a_{eH}/2$
5) preliminary results only
**Fig. 1:** Spectrum of Ne+(p-H_2)_c, nearest neighbour relaxation

**Fig. 2:** Spectrum of Ne+(p-H)_c, four shells relax

**Fig. 3:** p-H_2+(Ne)_c,
- --- c=0
- --- c=0,1, nearest neighbour relax
- ---- c=0,1, four shells relax

**Fig. 4:** p-H_2+(H)_c
- --- c=0
- --- c=0,05
- ---- c=0,1