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Room-Temperature Second-Order Raman Spectra of CsCl, CsBr, and CsI[†]

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The room-temperature Raman spectra of CsCl, CsBr, and CsI have been computed from a simple, combined density-of-states approximation. Calculations have been made for four different model potential functions and compared with experiment in the cases of CsBr and CsI. In this way it is found that one of the variations, called the DD(−) model, is the most satisfactory. The agreement with the observed spectra is surprisingly close when one considers that no allowance has been made for variations in the elements of the Raman polarizability tensor.

I. INTRODUCTION

THE advent of highly monochromatic laser sources has led to a renewed interest in the study of Raman scattering and, in particular, raises the possibility of definitive measurements of second-order spectra. This is particularly desirable in the case of the alkali halides, since, with the exception of the work of Welsh, Crawford, and Staple[1] on NaCl, the measurements made on these crystals using conventional mercury arc sources leave much to be desired.

As an obvious stimulus to such definitive measurements it is the purpose of this paper to present computed theoretical second-order spectra. We have in fact already done this in an earlier paper,[2] but the results given there were only appropriate to 0°K, and it is by no means certain that these can be directly compared with experimental spectra taken at room temperature (300°K). Thus the object of this paper is to present computed room-temperature spectra, and, in this, it is complementary to our earlier paper.[2] In addition, the number of theoretical models considered for each salt is greater, and another object is to decide which model is most realistic. In this respect the present paper also complements recent work[3] on the lattice dynamics and specific heat data of these compounds. In this work we find that it is not possible to decide unambiguously on the basis of specific heat data between two of the four theoretical models we use, and it is in the hope of resolving this question that we turn to second-order Raman spectra.

The second-order Raman effect is the inelastic scattering of photons by a crystal with the creation or destruction of two phonons, or the destruction of one phonon with the creation of a second. In all three cases the phonons involved are constrained by crystal momentum conservation to have equal and opposite wave vectors $\mathbf{q}$ and $-\mathbf{q}$. Moreover, the two processes involving phonon destruction can only take place at finite temperatures.

In the case of the alkali halide crystals, where the lattice sites are centers of inversion symmetry, second-order scattering is the lowest-order allowed Raman process.

II. METHOD OF CALCULATION

Strictly speaking, the Raman scattering cross section is a product of polarizability tensors and a density of final states, but we shall make the same simplifying assumption as we made in our earlier work,[2] namely that the polarizability tensors are constants. How justifiable this is, is not known, and we hope in a later paper to present the results of calculations made with specific polarizabilities; but, for the present, we shall continue to assume that the observed spectra are determined by the densities of final states.

Thus we compute a combined density of states $\rho(\omega)$ (omitting difference bands) given by

$$\rho(\omega)=\frac{1}{\Delta\omega}\sum_{\mathbf{q},j,j'}\int_{\omega}^{\omega+\Delta\omega}d\omega(n_j^{\mathbf{q}}+1)(n_{j'}^{-\mathbf{q}}+1)\times\delta(\omega-\omega_j^{\mathbf{q}}-\omega_{j'}^{-\mathbf{q}})+n_j^{\mathbf{q}}n_{j'}^{-\mathbf{q}}\delta(\omega+\omega_j^{\mathbf{q}}+\omega_{j'}^{-\mathbf{q}}),$$

where the n's are phonon occupation numbers appropriate to 300°K and $\omega_j^{\mathbf{q}}$ is the angular frequency of the phonon wave vector $\mathbf{q}$ belonging to the jth branch ($j=1$ to 6). In practice we can only deal with a discrete sample of $\mathbf{q}$ vectors and the sample used is the same as that employed in our other work[2,3] consisting of 64 000 points in the first zone. In each case, we first construct a histogram of $\rho(\omega)$ with $\Delta\omega$ deliberately chosen to be too small, then to the irregular steps so obtained we fit a sequence of Gaussians, each having the same height as a given step. By adjusting the common half-width of the Gaussians, a continuous smooth

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[†] Work performed in part under the auspices of the U. S. Atomic Energy Commission.

[1] H. L. Welsh, M. F. Crawford, and W. J. Staple, Nature **164**, 737 (1949).

[2] A. M. Karo, J. R. Hardy, and I. Morrison, J. Phys. (Paris) **26**, 668 (1965).

[3] J. R. Hardy and A. M. Karo, Phys. Rev. (to be published).

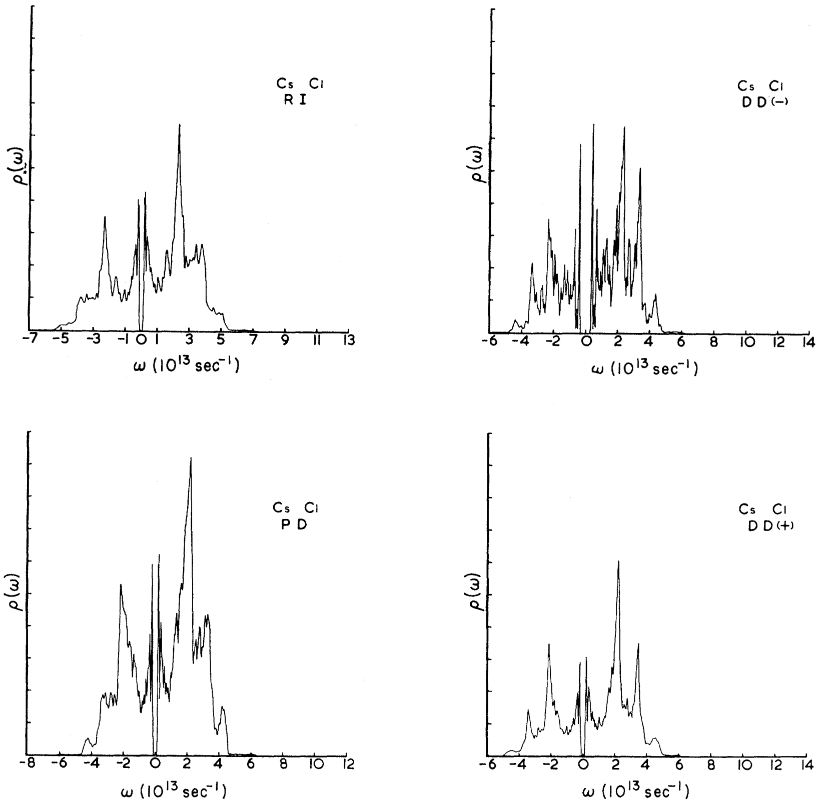

FIG. 1. Combined densities of states for all four potential options for CsCl.

curve can be obtained. We have used this technique elsewhere[3] and found that it reveals considerably more detail than does simple histogramming.

III. MODELS USED

The models used in the present work are described in detail elsewhere[3] and we only summarize their features here.

Four variations have been considered for each compound. In all four cases it has been assumed that the short-range repulsive interactions, which hold the ions apart, are effective between nearest neighbors alone. The differences lie in the way that the ionic polarization, and thus the dipole-dipole part of the dynamical matrix the roots of whose eigenvalues give the phonon frequencies, has been treated.

In the first variation, the rigid-ion (RI) model, the ions are assumed to displace as rigid point charges.

In the second variation, the polarization-dipole (PD) model, the ions are allowed to polarize and are assumed to acquire electronic dipole moments at their centers which are given by the products of the effective fields at these points and the self-consistent polarizabilities.

In the third variation it is assumed that, as well as exhibiting a field-induced polarization, the negative ions are also deformed by the short-range repulsion and thus acquire additional dipoles—the *deformation dipoles*. These dipoles are assumed to experience the fields at the negative ion centers, and we refer to this as the DD(−) variation.

The last variation is almost the same as DD(−) except that the deformation dipoles, although still confined to the negative ions, are assumed to experience the fields at the positive ion centers. This is the DD(+) variation. It is these last two variations which are hard to distinguish between on the basis of specific heat data,[3] even though they lead to very different frequency spectra. Consequently one may also hope that they will produce markedly different combined densities of states, and if this is the case, to distinguish between them by comparison with observed second-order Raman spectra.

The input parameters for the various calculations have been listed elsewhere,[3] the constants being those appropriate to room temperature (RT).

IV. RESULTS

In Figs. 1–3 we show the resultant combined densities of states for all four options, first for CsCl, then for CsBr, and finally for CsI. Then in Fig. 4 we show the observed second-order Raman spectra of CsBr[4] and CsI.[5] The corresponding spectrum of CsCl has recently

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[4] A. I. Stekhanov, A. P. Korol'Kov, and M. B. Eliashberg, Fiz. Tverd. Tela 4, 1290 (1962) [English transl.: Soviet Phys.—Solid State 4, 945 (1962)]. See also P. S. Narayan, Proc. Indian Acad. Sci. **42A**, 303 (1955).

[5] N. Krishnamurthy and R. S. Krishnan, Indian J. Pure Appl. Phys. **1**, 239 (1963).

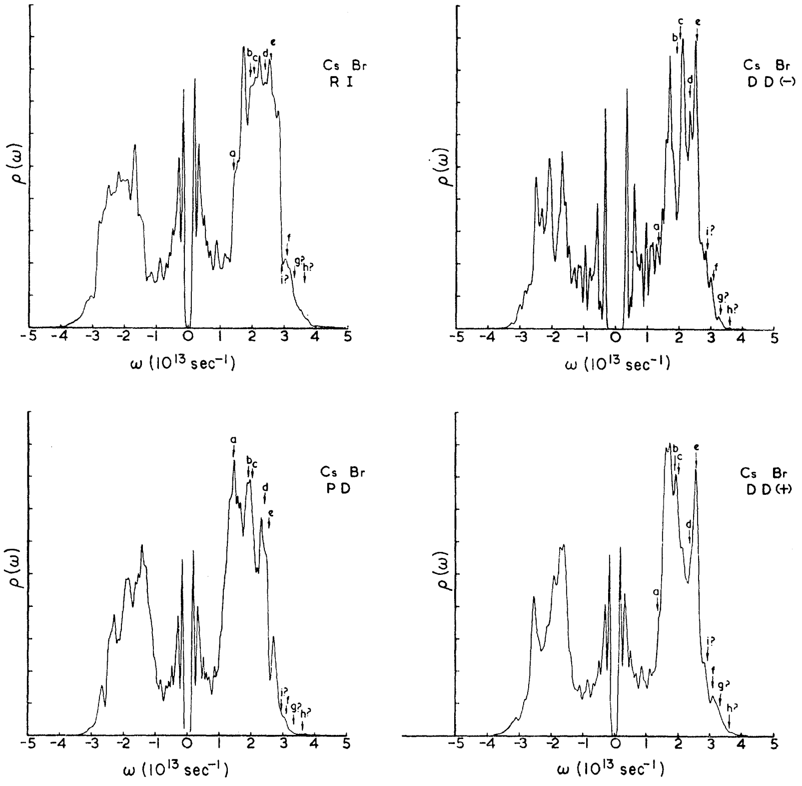

FIG. 2. Combined densities of states for the various potential options for CsBr. Positions of features of the observed spectrum are shown by *a*, *b*, *c*, etc.

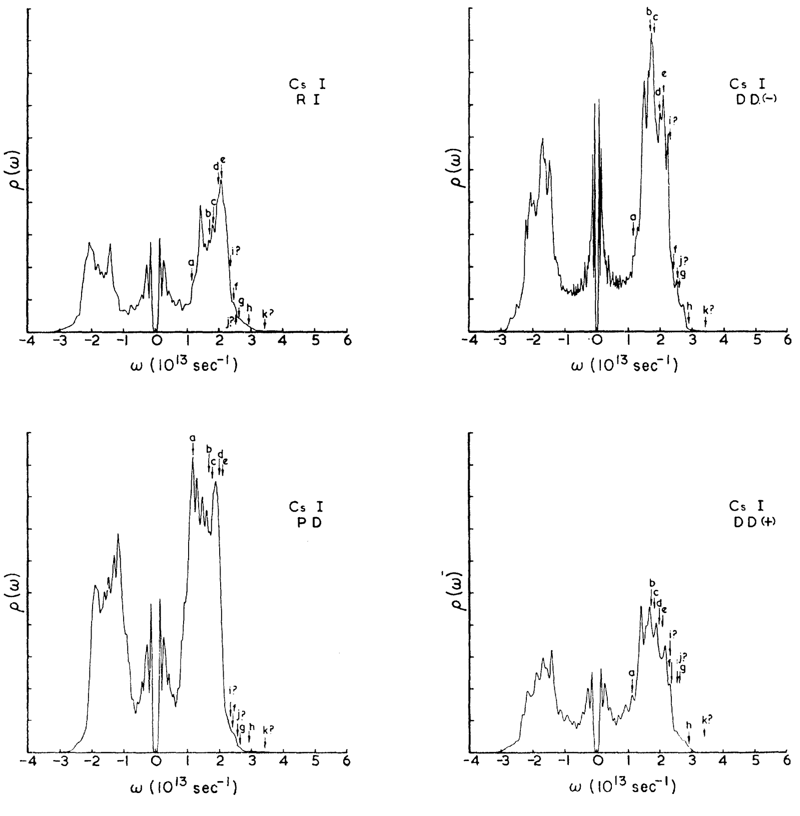

FIG. 3. Combined densities of states for CsI for the various potentials. Positions of features of the observed spectrum are shown by *a*, *b*, *c*, etc.

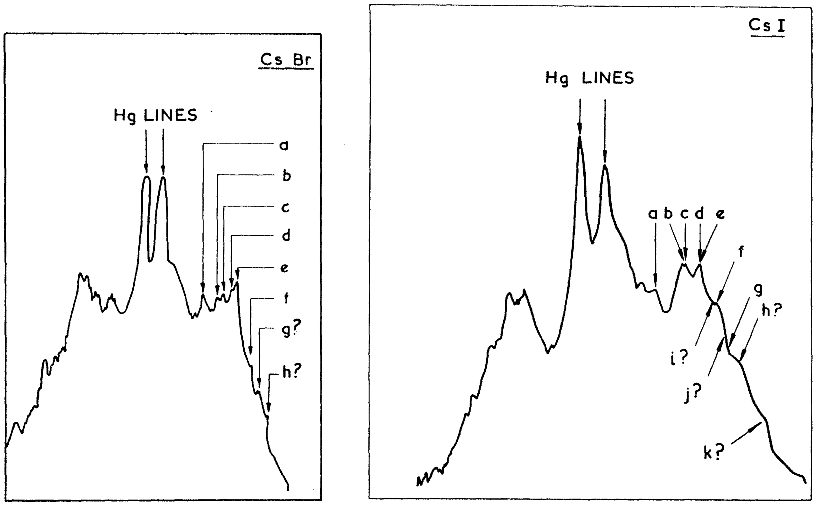

FIG. 4. Microphotometer records of the second-order room-temperature Raman spectra of CsBr (Ref. 4) and CsI (Ref. 5). The various distinct features of the combination bands are labeled to correspond with those in Figs. 2 and 3.

been measured,[6] but is not reproduced in this reference, and we shall therefore confine our discussion to CsBr and CsI. For purposes of comparison we have labeled the various observed features by *a*, *b*, etc., and their positions are also shown on all the computed spectra of Figs. 2 and 3. Any feature marked with a ? is either doubtful or a possible third-order line.

A. CsBr

The main features of the observed spectrum[4] are the peaks *a*, *b*, *c*, and *e*. Of the computed spectra only the PD curve shows a strong peak at *a*, but the remainder of this spectrum shows little resemblance to the observed curve; in particular the strong peak *e* is missing. The RI spectrum obviously bears no resemblance to the observed spectrum, and one is left to choose between DD(+) and DD(−). Of the two, DD(−) seems to bear the closest resemblance to the observed spectrum, reproducing the final strong peak *e* and the shoulder *d* on its low-frequency side remarkably well. At the low-frequency end, both spectra have weak peaks near the position of *a* and both have peaks near the *b*, *c* doublet. (It should be said that the observed doublet structure is questionable; all that can really be said is that there is a single broad peak.) However, both computed spectra show a strong peak on the low-frequency side of the *b*, *c* doublet which is unobserved. In the case of the DD(−) spectrum this is a TO(X)+TA(X) combination. It is quite likely that this occurs at too low a frequency because of our failure to include second-neighbor short-range interactions in the dynamical matrix, which would tend to raise the TO frequency.

Thus, on balance, one can say that the observed spectrum is best reproduced by the DD(−) model, and bearing in mind that no allowance has been made for variations in the polarizability tensors, the agreement with the observed spectrum is really quite close. The probable reason for this has been discussed elsewhere.[7] In this reference a detailed critical point assignment of the various computed features has been made, and this reveals that the various peaks are generally superpositions of critical points coming from several symmetry points in the first zone. For this reason one expects that variations in the polarizability tensors will tend to be averaged out.

B. CsI

In this case the observed spectrum[5] is somewhat better, and the main features of the spectrum are a peak *a* and two pairs of very close doublets *b*, *c* and *d*,*e* of about equal intensity. The RI spectrum completely fails to reproduce this doublet structure, with the first doublet only appearing as weak structure on the low-frequency side of a strong single peak. The PD spectrum is even worse with the doublet structure totally absent. The DD(+) spectrum is a little better, giving something like *b*, *c* but failing to reproduce *d*,*e*. The DD(−) spectrum, on the other hand, is very much better giving both doublets reasonably well. Once again the first strong peak of the computed spectrum, the TO(X)+TA(X) combination, seems to occur at too low a frequency, and again this is likely to be due to the neglect of second-neighbor forces. Also, the peak *a* is not well reproduced. However, on balance, one can say that the best fit to the observed spectrum is provided by the DD(−) model.

V. CONCLUSION

We have presented calculations of the room-temperature second-order Raman spectra of CsCl, CsBr, and

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[6] A. I. Stekhanov and A. P. Korol'Kov, Fiz. Tverd. Tela **8**, 920 (1966) [English transl.: Soviet Phys.—Solid State **8**, 734 (1966)].

[7] J. R. Hardy, in *Phonons*, edited by R. W. H. Stevenson (Oliver and Boyd, Ltd., London, 1966), p. 245.

CsI. These calculations have been based on a simple, combined density-of-states approximation. For CsBr and CsI comparison with experiment leads to the conclusion that, of all four model potential functions we have used, the DD(−) variation is the most satisfactory. For this variation the densities of states reproduce the observed spectra quite closely. This suggests that the behavior of the Raman polarizability tensor is of secondary importance in determining the observed spectra, but we hope to test this in the future by making calculations with explicit forms for the elements of this tensor included.

The computed spectra show considerable fine detail, and it would be highly desirable to have available for comparison really definitive experimental spectra taken with the highest possible resolution. It is also noteworthy that the theory predicts a great deal of sharp fine-structure in the low-frequency region, a region which is obscured in the experimental spectra by the tails on the exciting lines. One hopes that with laser sources it should be possible to examine this region.

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Lattice Thermal Conductivity in Disordered Harmonic and Anharmonic Crystal Models*

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Results of numerical calculations of energy transport in one- and two-dimensional lattice models are reported. Nearest-neighbor harmonic or anharmonic forces were used in randomly disordered mixtures of two different atomic masses. Opposite ends of the lattices were in contact with thermal reservoirs, which transfer energy impulsively at random times to the end atoms. A computer was used to solve the equations of motion of the lattice and to compute the heat current and thermal gradient. The thermal conductivity obtained shows the expected dependence on alloy composition. Except for nearly monatomic lattices, the calculations give larger heat conductivities for anharmonic lattices than for harmonic ones. A qualitative interpretation of these results, dependent upon the nature of the normal modes of disordered crystals, is given.

I. INTRODUCTION

In this paper we report the results of some numerical experiments which we have performed on certain simple lattice models. Our aim has been to study the effects of anharmonicity and of disorder on thermal resistance, separately and in combination. Our principal result is that an increase in anharmonicity usually produces a decrease in thermal resistance.

According to existing theories of thermal conductivity,[1] which stem from the ideas of Debye[2] and Peierls,[3] thermal resistance is caused by scattering of phonons. Impurities and anharmonicities provide two independent scattering mechanisms. One would therefore expect, and indeed existing theory[1] predicts, that their contributions to the thermal resistance should be more or less additive.

Our results are not consistent with this prediction, except possibly in the limit of very small impurity concentration, where the impurities and the anharmonicity may be considered to be perturbations on the ordered harmonic lattice. In this limit the idea of a phonon gas with weak impurity and phonon-phonon interactions is valid, because the lifetimes of the phonons are long compared to their periods.

A Boltzmann equation for the phonon distribution function, with collision terms arising from anharmonicity and from impurities, leads to expressions for the thermal resistance which increase with increasing anharmonicity. We believe that the opposite behavior of our numerical results indicate that the phonon gas is a useful concept only for very low impurity concentrations.

Our approach, which is purely classical, uses a specific model for the lattice in interaction with thermal reservoirs at the two ends. The model and the method by which we numerically solve the equations of motion for the system until a steady state is reached are described in Sec. II.

This numerical experiment yields much raw data, namely, the position and velocity of each atom in the

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[1] J. Callaway, Phys. Rev. **113**, 1046 (1959); P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

[2] P. Debye, *Vorträge Über die Kinetische Theorie der Materie und der Elektrizität* (Teubner, Berlin, 1914).

[3] R. E. Peierls, Ann. Physik 3, 1055 (1929).