PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Effect of Anharmonic Libron Interactions on the Single-Libron Spectrum of Solid H_2 and D_2 †

Cornelius F. Coll, III* and A. Brooks Harris
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 19 January 1971)

The effects of interactions between the elementary excitations (librons) in the orientationally ordered phase of solid H_2 and D_2 are studied using diagrammatic perturbation theory. This formulation leads naturally to the construction of a renormalized dynamical matrix which includes all anharmonic effects. The cubic anharmonic interactions are by far the dominant ones, and we have calculated the energy shifts of each of the zero-wave-vector libron modes self-consistently to lowest order in the expansion parameter $1/z$, where $z=12$ is the number of nearest neighbors. We find the libron energies (in units of the electrostatic quadrupole-quadrupole coupling constant Γ) to be 11.29 (13.66), 14.07 (17.72), and 19.55 (29.04) with the corresponding harmonic values in parentheses. In contrast to the harmonic theory, these anharmonic results provide a striking fit to the observed Raman spectrum of solid H_2 and D_2 with reasonable values of Γ, e.g., $\Gamma=0.59\ \mathrm{cm}^{-1}$ for H_2 and $\Gamma=0.83\ \mathrm{cm}^{-1}$ for D_2. We develop an expression for the Raman intensities in terms of the single-libron spectral weight function. The group-theoretical simplifications in our calculations are discussed in detail in the appendices. The cubic anharmonicity is shown in the accompanying paper to lead to a two-libron spectrum which explains the appearance of "extra" high-energy lines in the Raman spectrum of solid hydrogen. These effects are shown to be included in the renormalized dynamical matrix in the present approximation. Sum rules for the Raman intensities are derived and are used to check the calculations.

I. INTRODUCTION

The analogy[1] between spin waves in a magnetic system and librational waves in solid hydrogen is a very direct and appealing one. In magnetic systems spin waves can be observed directly via inelastic scattering of neutrons,[2] and by means of this technique the validity of the concept of spin waves has been demonstrated beyond any doubt.[3] In principle, these observations should also demonstrate the presence of anharmonic interactions between the elementary excitations, since these interactions cause the energy of the elementary excitations to have a temperature dependence. Unfortunately, in the low-temperature regime where these anharmonic effects can be treated theoretically with the most confidence,[4] the resulting energy shifts are too small to be easily measured in most cases. It is probable, however, that recent experiments[5] on $CrBr_3$ or on layered antiferromagnets[6] will enable a convincing comparison to be made between the theoretical and observed anharmonic temperature-dependent shifts in the spin-wave energy. Another complementary method is to observe the two-magnon spectrum, as can best be done in antiferromagnets.[7] Here the two magnons are created on neighboring sites and their binding energy accounts for the difference between the energy of two free spin waves and the observed peak in the two-magnon density of states.[8,9] These observations directly confirm Dyson's model[10] of spin-wave interactions as applied to antiferromagnets. As we shall see, the situation with regard to the direct observation of anharmonic interactions between the elementary excitations is more favorable in solid hydrogen, and the aforementioned effects for magnetic systems have more important analogs in solid hydrogen. In this paper the effects of anharmonicity on the single-particle spectrum will be the subject of a detailed calculation. The results are modified slightly from those we reported previously.[11] The two-libron spectrum is discussed in the accompanying paper.[12]

Before continuing the discussion of the analogy between solid hydrogen and magnetic systems, let us review the experimental situation. By now it seems quite likely, both on theoretical[13] and experimental grounds,[14–18] that the dominant interactions between molecules are the electric quadrupole-quadrupole (EQQ) interactions. Based on this model, one can understand a variety of observations, such as specific heat[13,19–21] or $(\partial p/\partial T)_V$ measurements,[22,23] NMR splittings,[24–28] line shapes,[26,27,29,30] and relaxation times.[28,31–41] Thus, in contrast to magnetic systems, the interactions between molecules are fairly well established from first principles. It was therefore surprising that the observation[42] of the $k=0$ libron spectrum should show five lines[43] instead of three as one would have expected[44–50] for the assumed configuration of molecules on an fcc lattice with four molecules per unit cell.[51,52] Even the fit of the lowest three of these observed lines to the calculated single-libron spectrum was not satisfactory.[50] Several possible explanations for the observed Raman spectrum have been advanced. For instance, Hardy *et al.*[42,43] have suggested the possible existence of a distortion to a structure of lower symmetry. They also speculated on the possible importance of libron-phonon interactions.[43] Perhaps the most appealing suggestion was that by Elliott[53] and Nakamura and Miyagi[50] that the "extra" two lines in the observed spectrum were due to two-libron excitations. Neither author was able to give a plausible mechanism for such a process, however. More recently, Coll *et al.*[11] have proposed a mechanism based on the existence of cubic anharmonicity which permits a virtual libron to decay into two final-state librons. This explanation was motivated by our previous observation[49] that the cubic libron-libron interactions in solid hydrogen are quite large.

Let us consider the effect of these large cubic libron-libron interactions in terms of the analogy between librons in solid hydrogen and spin waves in magnetic systems. In magnetic systems cubic magnon-magnon interactions arise mainly from dipolar interactions,[54,55] and hence they usually have a negligible effect on the excitation spectrum. As mentioned above, the effect of the quartic magnon-magnon interactions, which arise from the anharmonicity inherent in the Heisenberg Hamiltonian, is small at low temperatures.[10] Likewise, in an antiferromagnet, zero-point effects on the magnon-energies due to quartic magnon-magnon interactions are generally rather small.[54,55] In contrast, the effects of the cubic libron-libron interactions on the libron energies in solid hydrogen are quite large,[49] leading to energy shifts of order 20%. Since these interactions cause mixing of one- and two-libron states, they permit the observation of two-libron states in the nominally single-libron spectrum. As reported earlier,[11] the large energy shifts and extra lines caused by these interactions are in striking agreement with the observed five-line Raman spectrum[43] and hence clarify its interpretation.

Since this paper is concerned with the calculation of the effects of libron-libron interactions on the single-libron energies, let us review the status of various approximations which have been used to treat the analogous magnetic problem. A commonly used approach, qualitatively valid over a wide range of temperature, is the random-phase approximation (RPA). Here, since each spin is treated as if it precesses in the average field of its neighbors, one predicts that the excitation energy $\epsilon_{\vec{k}}$ is given as[56]

$$\epsilon_{\vec{k}} = \epsilon^0_{\vec{k}}(\langle S_z \rangle / S) \tag{1.1}$$

when the effects of anharmonicity are included. Here $\epsilon^0_{\vec{k}}$ is the unperturbed magnon energy for wave vector $\vec{k}$, and $\langle S_z \rangle$ is the thermodynamic average of the z component of spin. Owing to zero-point motion we see that in an antiferromagnet the RPA predicts that

$$\epsilon_{\vec{k}} / \epsilon^0_{\vec{k}} < 1 \ . \tag{1.2}$$

On the other hand, for the ferromagnet, Dyson's rigorous result, obtained using diagrammatic perturbation theory, gives essentially[10]

$$\epsilon_{\vec{k}} = \epsilon^0_{\vec{k}} [U(T)/U_0] , \tag{1.3}$$

where $U(T)$ is the internal energy at temperature T and U_0 is the ground-state energy. The result in Eq. (1.3) is physically more plausible than that of Eq. (1.1), since the former takes better account of the strong correlations between neighboring spins. A clear physical explanation of these effects is given by Keffer and Loudon.[57] These results are also qualitatively correct for the antiferromagnet, as can be seen from Oguchi's formal analysis,[58] providing we interpret U_0 as the energy of the Néel state, $-Nz|J|S^2$. However, it is clear from the variational principle and also from Ref. 58 that $U(0)$, the true ground-state energy, is less than U_0, so that $U(0)/U_0 > 1$. Thus, at zero temperature one expects

$$\epsilon_{\vec{k}} / \epsilon^0_{\vec{k}} > 1 \ , \tag{1.4}$$

as has been found.[58] Hence the RPA cannot be used to discuss zero-point effects.

This discussion has obvious implication for solid hydrogen. Since the libron energy gap is very large,[44–50] thermal effects will be small in comparison to zero-point effects except possibly very near the order-disorder transition. Thus, except near the transition, the RPA will be qualitatively incorrect and we must rely on perturbation theory. In fact, the RPA is even worse for solid hydrogen than for magnetic systems, because it neglects completely the effects of the cubic-anharmonic terms. This same shortcoming has been noted and overcome by Horner[59] in his treatment of phonons in solid helium. His theory resembles ours in that inclusion of cubic anharmonicity self-consistently in second-order perturbation theory leads to large single-phonon energy shifts and to the appearance of two-phonon excitations in the nominally single-phonon spectrum.

Higher-order effects have not been treated in detail for the anharmonic phonon system, and the expansion parameter has not been identified with any certainty. For the system of interacting spin waves governed by the Heisenberg Hamiltonian the parameter $1/z$, where z is the number of nearest neighbors, can be identified as the expansion parameter in cases where an expansion in powers of $1/S$ is not suitable.[60] This scheme is clearly advantageous here, since the system of ($J=1$) molecules is isomorphic to a spin-1 magnetic system.

This formulation has several advantages. First, by identifying $1/z$ as an expansion parameter we are able to estimate that correction terms beyond second-order perturbation theory will not qualitatively affect our results. Second, it enables us to give many analytic results. Finally, as shown elsewhere[60] for magnetic systems, this formulation seems to eliminate the kinematic effects of those multiexcitation boson states which have no physical reality.

Briefly, this paper is organized as follows. In Sec. II we discuss the model we use in which the molecules are treated as rigid rotators on a rigid lattice. The Hamiltonian describing molecular rotations is expressed in terms of boson operators so that conventional many-body techniques can be used. We discuss the approximation scheme upon which our calculations are based and argue that the approximation of low libron density leads naturally to the $1/z$ expansion. In Sec. III we introduce the Green's-function formalism. In the present calculation the normal-mode structure necessitates the use of matrix Green's functions. We show that the quasiparticle energies may be determined from a dynamical matrix which incorporates anharmonic effects. In Sec. IV we present results within various approximations for the average libron energy, the libron energies at zero wave vector, and the Raman intensities at zero wave vector. In Sec. V we compare the results of our calculations with the Raman data[42,43] for the zero-wave-vector modes and with the thermodynamic data[20,23] for the average libron energy gap. In conclusion the various experimental determinations of the EQQ coupling constant and proposed topics for future study are discussed.

Appendix A deals with the diagonalization of the dynamical matrix. Here group-theoretical considerations are used to reduce the anharmonic dynamical matrix to block-diagonal form for zero wave vector. In Appendix B the Raman intensities of the normal modes are calculated by expressing them in terms of the spectral weight functions of the Green's functions evaluated in Sec. III. The symmetry properties of the Green's functions are discussed in Appendix C and sum rules for the Raman intensity are obtained in Appendix D.

II. DESCRIPTION OF MODEL AND APPROXIMATION SCHEME

A. Description of Model

Solid hydrogen is a molecular crystal in which the molecules interact mainly via weak long-range forces such as van der Waals interactions. Many of the bulk properties, such as the compressibility,[61] appear to be insensitive to the orientational configuration of the molecules. This fact is partly due to the relative weakness of the orientational interactions and partly due to the fact that such anisotropic interactions tend to cancel[13] in the highly symmetric crystalline environment. For these reasons it seems clear that it is possible to treat phonons and molecular rotations as separate entities. The interactions between phonons and molecular rotations have been shown[62–64] to lead to renormalizations of the orientational interactions. Although these renormalizations change the strength of the EQQ interactions, they do not alter their angular dependence.[64] As a result, the EQQ coupling parameter Γ_0 [see Eq. (2.5) below] should be replaced by an effective value Γ which is about 15–20% smaller than Γ_0.[62–64] Apart from this renormalization phonons will be completely ignored, and we shall henceforth treat the molecules as if they were on a rigid lattice.

As mentioned above, we consider it established that the orientational coupling between hydrogen molecules is primarily of EQQ character. We shall neglect the much smaller valence and dispersion terms in the interaction between molecules.[13] These EQQ interactions are much smaller than the energy differences between adjacent kinetic-energy levels of the freely rotating hydrogen molecule. As a result, the hydrogen molecule is a quantum rotator in the sense that the rotational angular momentum J_i of the ith molecule is essentially a good quantum number.

Let us consider the possible values of the J_i's. As is well known, different parity rotational wave functions must be combined with different parity nuclear spin functions. Thus even and odd J molecules are essentially different species. Although there is a gradual conversion towards the lower energy, i.e., $J=0$, species, we may consider the solid as being a random alloy with a fixed proportion of even and odd J molecules.[65] Since we are only interested in low temperatures, all even J molecules have $J=0$ and all odd J molecules have $J=1$. Such an alloy of $(J=1)$ and $(J=0)$ molecules is similar to a magnetic alloy consisting of spin-1 and spin-zero ions.[1] Since the problem of excitations in such an alloy is not completely resolved, we shall confine our attention to the pure $(J=1)$ solid, and make phenomenological corrections when applying our results to nearly pure $(J=1)$ alloys.

In this paper we shall consider only the orientationally ordered phase. According to x-ray diffraction[66] and neutron-scattering experiments[67] the crystal structure is face-centered cubic (fcc). The probable ground-state orientations of molecules on an fcc lattice interacting by means of EQQ forces were obtained classically by Nagai and Nakamura,[51] who found a four sublattice structure. On different sublattices the quadrupoles are aligned along different $\langle 111 \rangle$ directions relative to the cubic axes. In a quantum-mechanical treatment[52] the equilibrium orientation of a quadrupole becomes the quantization axis relative to which the molecule in question has $J_z \approx 0$. Thus solid hydrogen in the orientationally ordered phase can be described as a simple-cubic lattice with a basis of four molecules per unit cell, whose space group is $Pa3(T_h^6)$.

B. Orientational Hamiltonian

The orientational Hamiltonian is of the form

$$\mathcal{H} = \frac{1}{2}\sum_{i,j} V_{ij}(\hat{\Omega}_i, \hat{\Omega}_j) , \qquad (2.1)$$

where $\hat{\Omega}_i$ specifies the orientation of the ith molecule relative to the crystal axis. For EQQ interactions the Hamiltonian V_{ij} may be written as[14]

$$V_{ij} = \tfrac{20}{9}\pi(70\pi)^{1/2}\left(\frac{6e^2Q^2}{25R_{ij}^5}\right)\sum_{M,N} C(224; M, N) \times Y_2^M(\hat{\Omega}_i)Y_2^N(\hat{\Omega}_j)Y_4^{M+N}(\hat{\Omega}_{ij})^* , \qquad (2.2)$$

where eQ is the molecular quadrupole moment[68] and $\hat{\Omega}_{ij}$ denotes the orientation of the vector connecting the ith and jth molecules relative to the crystal axes. We use the phase convention of Rose[69] for the spherical harmonics Y_J^M and the Clebsch-Gordan coefficients $C(J_1J_2J_3; M, M')$.

Following Raich and Etters[46] we write the EQQ Hamiltonian so that the orientation of each molecule is specified relative to its equilibrium orientation. This is achieved by writing in Eq. (2.2)

$$Y_2^M(\hat{\Omega}_i) = \sum_N D_{MN}^{(2)}(\hat{\chi}_i)^* Y_2^N(\hat{\omega}_i) , \qquad (2.3)$$

where $D_{MN}^{(2)}(\hat{\chi}_i)$ is a rotation matrix, $\hat{\chi}_i \equiv (\alpha_i, \beta_i, \gamma_i)$ are the Euler angles[69] specifying the orientation of the local (equilibrium) axes relative to the cubic-crystal axes, and the orientation of the ith molecule relative to its local axes is denoted by $\hat{\omega}_i \equiv (\theta_i, \varphi_i)$. The local axes, which are identical for all sites on the same simple-cubic sublattice, are given in Table I along with the positions of the sublattices relative to the origin of the unit cell. Thus the Hamiltonian is written in terms of the spherical harmonics referred to the local axes as

$$\mathcal{H} = \sum_{i,j} \tfrac{10}{9}\pi(70\pi)^{1/2}\Gamma_{ij}\sum_{M,M',N,N'} C(224; N, N') \times D_{NM}^{(2)}(\hat{\chi}_i)^* D_{N'M'}^{(2)}(\hat{\chi}_j)^* Y_2^M(\hat{\omega}_i)Y_2^{M'}(\hat{\omega}_j)Y_4^{N+N'}(\hat{\Omega}_{ij})^* , \qquad (2.4)$$

TABLE I. Position and equilibrium orientation of sites.

α[a]	Sublattice[b]	Direction of z axis	Direction of x axis
1	$\frac{1}{2}a(0,0,0)$	[111]	$[11\bar{2}]$
2	$\frac{1}{2}a(1,1,0)$	$[\bar{1}11]$	$[\bar{1}1\bar{2}]$
3	$\frac{1}{2}a(0,1,1)$	$[1\bar{1}1]$	$[1\bar{1}\bar{2}]$
4	$\frac{1}{2}a(1,0,1)$	$[11\bar{1}]$	$[\bar{1}\bar{1}\bar{2}]$

[a]Here α labels the sublattice.
[b]Here $a = \sqrt{2}R_0$, where R_0 is the nearest-neighbor separation.

where we have used the conventional notation Γ_{ij} for the EQQ coupling parameter:

$$\Gamma_{ij} = \frac{6e^2Q^2}{25R_{ij}^5} \equiv \Gamma_0\left(\frac{R_0}{R_{ij}}\right)^5 , \qquad (2.5)$$

where R_0 is the distance between nearest neighbors. As mentioned above, due to phonon renormalization[62-64] we should replace Γ_0 by an effective value Γ.

Within the manifold of constant J_i we may, by virtue of the Wigner-Eckart theorem, replace the spherical harmonic $Y_J^M(\hat{\omega}_i)$ by a tensor operator which is a function of J_i:

$$Y_2^M(\hat{\omega}_i) = A_M O_i^M(J_i) , \qquad (2.6)$$

with

$$A_0 = -\left(\tfrac{9}{20\pi}\right)^{1/2}, \qquad (2.7a)$$

$$A_{\pm1} = \left(\tfrac{3}{20\pi}\right)^{1/2}, \qquad (2.7b)$$

$$A_{\pm2} = -\left(\tfrac{3}{10\pi}\right)^{1/2} , \qquad (2.7c)$$

and

$$O_i^0 = J_{zi}^2 - \tfrac{2}{3} , \qquad (2.8a)$$

$$O_i^{\pm1} = \pm (J_{zi}J_{\pm i} + J_{\pm i}J_{zi})/(2)^{1/2} , \qquad (2.8b)$$

$$O_i^{\pm2} = \tfrac{1}{2}J_{\pm i}^2 , \qquad (2.8c)$$

where

$$J_{\pm i} = J_{xi} \pm iJ_{yi} . \qquad (2.8d)$$

Within the subspace of $J_i = 1$ the EQQ Hamiltonian becomes

$$\mathcal{H} = \frac{1}{2}\sum_{i,j}\sum_{M,N} \zeta_{ij}^{M,N} O_i^M O_j^N , \qquad (2.9)$$

with

$$\zeta_{ij}^{M,N} = \tfrac{20}{9}\pi(70\pi)^{1/2}\Gamma_{ij}A_M A_N \sum_{M',N'} C(224; M', N') \times Y_4^{M'+N'}(\hat{\Omega}_{ij})^* D_{M'M}^{(2)}(\hat{\chi}_i)^* D_{N'N}^{(2)}(\hat{\chi}_j)^* . \qquad (2.10)$$

The values of the ζ's for a particular nearest-neighboring pair are given in the accompanying paper.[12] Values of these constants for other pairs of nearest neighbors can be found by applying the symmetry operators, as is discussed in Appendix B of Ref. 49. The notation in Eqs. (2.7)-(2.10) is somewhat different from that used previously.[11,46,48,49] Specifically, the $\zeta_{ij}^{M,N}$ are related to the $\gamma_{ij}^{M,N}$ of the references cited by

$$\zeta_{ij}^{M,N} = 2\gamma_{ij}^{M,N} g(M)g(N) , \qquad (2.11)$$

where $g(\pm 2) = 2$, $g(\pm 1) = \pm\sqrt{2}$, and $g(0) = 3$. The motivation for introducing this notation is that we thereby avoid, insofar as is possible, the appearance of arbitrary numerical coefficients in our equations.

In the case of the antiferromagnet the classical ground state is related to the quantum-mechanical Néel state in a particularly simple way. Likewise, here the Néel state is one in which $J_{zi}=0$ relative to the local axes. Thus, in order to describe deviations from the Néel state, we expand the Hamiltonian about $J_{zi}=0$. The correct low-temperature behavior for magnetic systems has been shown to be most readily formulated using diagrammatic perturbation theory. For such calculations, the simplest formalism employing boson operators is the Dyson-Maléev transformation.[10,70] Here we use a similar transformation from angular-momentum operators to boson operators c_{i+} and c_{i-}:

$$O_i^0=(c_{i+}^\dagger c_{i+}+c_{i-}^\dagger c_{i-})-\tfrac{2}{3}\ , \tag{2.12a}$$

$$O_i^1=[c_{i+}^\dagger(1-c_{i+}^\dagger c_{i+}-c_{i-}^\dagger c_{i-})-(1-c_{i+}^\dagger c_{i+}-c_{i-}^\dagger c_{i-})c_{i-}]\ , \tag{2.12b}$$

$$O_i^{-1}=-(O_i^1)^\dagger\ , \tag{2.12c}$$

$$O_i^2=c_{i+}^\dagger c_{i-}\ , \tag{2.12d}$$

$$O_i^{-2}=(O_i^2)^\dagger\ , \tag{2.12e}$$

and we shall set

$$c_{iM}=c_{i+}\ ,\quad M=1 \tag{2.12f}$$

$$=c_{i-}\ ,\quad M=-1. \tag{2.12g}$$

We interpret $c_{iM}^\dagger$ as the operators which create excited states for which $J_{zi}=M$ when applied to molecules in the ground state. As we shall see, this notation is convenient in that it allows us to display explicitly the symmetry between M and $-M$. The transformation given in Eq. (2.12) correctly reproduces the matrix elements of the angular-momentum operators within the manifold of three states per molecule which have physical significance. In addition, the factors in parentheses in Eq. (2.12b) ensure that the angular-momentum operators have no matrix elements connecting the physical and unphysical states. In this respect, the transformation given by Nakamura and Miyagi[50] in their Eq. (2.17) appears to be less suitable. Previously[49] we had used a less symmetrical, but simpler, transformation which led to a formally non-Hermitian Hamiltonian. Although that formulation is economical for a low-order discussion of the static properties, it leads to a loss of symmetry in the anharmonic dynamical matrix, which we avoid for convenience sake. Although the equivalence of the different transformations is not obvious, it does seem to hold for magnetic systems.[71]

If we introduce the above expressions into Eq. (2.9), we may classify the terms in the Hamiltonian according to the number of bosons operators involved as

$$\mathcal{H}=\hat{E}_0+\mathcal{H}_2+\sum_{n=3}^{6}V_n\ , \tag{2.13}$$

where $\hat{E}_0$ is the energy of the Néel state, $\mathcal{H}_2$ is the Hamiltonian quadratic in the boson operators, and V_n is the anharmonic term involving n boson operators. The quadratic Hamiltonian is given by

$$\mathcal{H}_2=-\frac{2}{3}\sum_{\substack{i,j\\M}}{}'\zeta_{ij}^{0,0}c_{iM}^\dagger c_{iM}-\sum_{\substack{i,j\\M,N}}{}'\zeta_{ij}^{M,-N}c_{iM}^\dagger c_{jN}+\frac{1}{2}\sum_{\substack{i,j\\M,N}}{}'(\zeta_{ij}^{M,N}c_{iM}^\dagger c_{jN}^\dagger+\zeta_{ij}^{M,N*}c_{iM}c_{jN})\ . \tag{2.14}$$

Here and below a prime on the summation indicates that the magnetic quantum number (e.g., M or N) is limited to the values ±1.

This Hamiltonian is identical to that of Raich and Etters[46] although the interpretation of the operators c_{i+} and c_{i-}, for which they use the notation a_i and b_i, respectively, is different, in that in their formalism these operators satisfy boson commutation relations only at zero temperature. The excitation spectrum of the quadratic Hamiltonian was obtained by Raich and Etters[46] and others,[45,47] who considered only interactions between nearest-neighboring molecules. As Berlinsky *et al.*[48] have pointed out, further-neighbor interactions have an important effect on the libron spectrum obtained from the quadratic Hamiltonian of Eq. (2.14). As noted in Ref. 48, the main effect of further-neighbor interactions is contained in $\zeta_{ij}^{0,0}$, where they lead to a renormalization of the average libron energy [see Eq. (2.19a) below]. The effect of further-neighbor interactions via the hopping terms involving $\zeta_{ij}^{M,M'}$ with $M^2+M'^2\neq0$ is much less significant. In the context of perturbation theory such effects are reflected in the lattice sums of the form $\sum_j|\zeta_{ij}^{M,M'}|^2$ [e.g., see Eq. (4.3) below], where they lead to negligible corrections, since $\zeta_{ij}^{M,M'}\sim R_{ij}^{-5}$. Similar reasoning allows us to restrict the anharmonic terms to nearest-neighbor interactions.

Within the approximation we shall use, V_5 and V_6 do not contribute, so they will not be considered explicitly. The expressions for V_3 and V_4 are

$$V_3=\sum_{\substack{i,j\\M,M',N}}{}'(\zeta_{ij}^{M-M',N}c_{iM}^\dagger c_{iM'}c_{jN}^\dagger+\zeta_{ij}^{M-M',N*}c_{iM'}^\dagger c_{iM}c_{jN})\ , \tag{2.15}$$

$$V_4=\frac{1}{2}\sum_{\substack{i,j\\M,M'\\N,N'}}{}'\zeta_{ij}^{M-M',N-N'}c_{iM}^\dagger c_{jN}^\dagger c_{iM'}c_{jN'}+\sum_{\substack{i,j\\M,M',N}}{}'(\zeta_{ij}^{M,-N}c_{iM}^\dagger c_{jM'}^\dagger c_{jM'}c_{jN}+\zeta_{ij}^{M,-N*}c_{iM}c_{jN}^\dagger c_{jM'}^\dagger c_{jM'})$$

$$- \sum_{\substack{i,j\\M,M',N}}{}' \left(\zeta_{i,j}^{M,N} c_{iM}^\dagger c_{jN}^\dagger c_{jM'}^\dagger c_{jM'} + \zeta_{ij}^{M,N*} c_{iM} c_{jM'}^\dagger c_{jM'} c_{jN}\right) . \qquad (2.16)$$

We shall study the effects of these anharmonic terms using perturbation theory.

C. 1/z Approximation Scheme

The deviation of the true ground state from the molecular field or Néel ground state can be measured by $\rho(0)$, the density of zero-point deviations. Here we define

$$\rho(T) = (4N_0)^{-1} \sum_{i,M}{}' \langle c_{iM}^\dagger c_{iM}\rangle_T , \qquad (2.17)$$

where N_0 is the number of unit cells and the bracket $\langle\ \rangle_T$ indicates a thermodynamic average at temperature T. Since the orientational system is nearly in the Néel state as long as the temperature is not too high, we expect that thermodynamic quantities can be expanded in powers of the deviations from the Néel state. In other words, we are treating a dilute gas of librons whose properties can be expanded in powers of their density $\rho(T)$. For such a treatment the diagrammatic formulation of perturbation theory developed by Bloch and deDominicis[72,73] is convenient. From their formulation it is clear that for each hole line in a diagram there corresponds a Bose factor, which is given approximately by

$$\Delta\rho \equiv \rho(T) - \rho(0) \approx [e^{E_L/kT} - 1]^{-1} ,$$

where E_L is the average libron energy. Thus the low-density (of librons) expansion naturally involves the two parameters $\rho(0)$ and $\Delta\rho$. Since the libron energy gap is rather large[42] ($E_L \sim 10\ \text{cm}^{-1}$), effects involving the thermal density of librons, $\Delta\rho$, will be quite small compared to the zero-temperature effects, except perhaps near the orientational ordering transition temperature. Thus, to examine low-temperature effects, we consider only those diagrams with no hole lines.

In order to classify in a consistent way diagrams with no hole lines, we note that the zero-point density of excitations, $\rho(0)$, is of order $1/z$, where z is the number of nearest neighbors.[60] This result is plausible, since it is known that the molecular field becomes exact in the limit of long-range forces. The explicit appearance of $1/z$ as an expansion parameter is achieved by taking the unperturbed Hamiltonian to consist of the molecular field terms, i.e., those terms diagonal in the number of excitations. We write these terms as

$$\mathcal{H}_{00} = E_0 \sum_{i,M}{}' c_{iM}^\dagger c_{iM} , \qquad (2.18)$$

where the molecular field energy E_0 is given as

$$E_0 = -\tfrac{2}{3} \sum_j \zeta_{ij}^{0,0} . \qquad (2.19a)$$

If the sum is restricted to nearest neighbors, one obtains $E_0 = 19\Gamma$. Taking account of further-neighbor interactions, Berlinsky *et al.*[48] found

$$E_0 = 21.2\Gamma . \qquad (2.19b)$$

We consider E_0 to be of order z $[O(z)]$ because z nearest neighbors contribute to this field. The perturbation then consists of those terms, which we denote by V_2, omitted from the harmonic Hamiltonian of Eq. (2.14) and the anharmonic terms V_3, V_4, etc. Terms in perturbation theory are classified according to their order in $1/z$ by the number of independent lattice sums involved: Sums over n independent lattice sites are considered to be of order z^n. The identification of $1/z$ as an expansion parameter enables us to estimate the effects of higher-order terms in perturbation theory. In addition, use of such a scheme probably preserves the kinematic properties of angular-momentum operators.[60] This view is supported by the agreement between the average libron energy as calculated in this paper using boson operators and that obtained in the accompanying paper[12] using angular-momentum operators.

III. CALCULATION

A. Formalism

In this subsection we shall introduce the temperature-dependent Green's functions[74] for the boson operators. The imaginary-time Green's functions $G_{\sigma\sigma'}(i, M; j, N; t)$ are defined for times in the interval $(0, -i\beta)$ as

$$G_{11}(i, M; j, N; t) = -i\langle c_{iM}(t) c_{jN}^\dagger(0)\rangle_T , \qquad (3.1a)$$

$$G_{12}(i, M; j, N; t) = -i\langle c_{iM}(t) c_{jN}(0)\rangle_T , \qquad (3.1b)$$

$$G_{21}(i, M; j, N; t) = -i\langle c_{iM}^\dagger(t) c_{jN}^\dagger(0)\rangle_T , \qquad (3.1c)$$

$$G_{22}(i, M; j, N; t) = -i\langle c_{iM}^\dagger(t) c_{jN}(0)\rangle_T , \qquad (3.1d)$$

and their temporal Fourier coefficients are

$$G_{\sigma\sigma'}(iM; jN; \mathfrak{z}_r) = \int_0^{-i\beta} G_{\sigma\sigma'}(iM; jN; t) e^{i\mathfrak{z}_r t}\, dt , \qquad (3.2)$$

where $\mathfrak{z}_r = i\pi r/\beta$, with r an even integer.[75] These Green's functions do not have a simple structure, because they do not refer to individual normal modes. The unperturbed normal modes are obtained by diagonalizing the quadratic Hamiltonian $\mathcal{H}_2$ given in Eq. (2.14). These unperturbed normal modes are created by linear combinations of the $c_{iM}^\dagger$ and c_{iM}, and it can be shown that the normal-mode frequencies and creation operators are found by diagonalizing an 8×8 dynamical matrix.[44-47] We shall eventually construct a renormalized dynamical matrix which includes anharmonic effects.[76] In this way we avoid many of the algebraic complexities caused by the normal-mode diagonalization. To treat this normal-mode structure we have introduced matrix Green's functions analogous to those of the Nambu formalism of superconductivity.[77] In matrix notation the self-energy $\underline{M}$ is defined via a Dyson equation as

$$\underline{G} = \underline{G}^0 + \underline{G}^0 \underline{M}\,\underline{G}\,, \tag{3.3}$$

where $\underline{G}^0$ is the Green's function for the molecular field Hamiltonian of Eq. (2.18). Explicitly Eq. (3.3) reads

$$G_{\sigma\mu}(i, M; j, N; \mathfrak{z}_r) = G^0_{\sigma\mu}(i, M; j, N; \mathfrak{z}_r) + \sum_{\sigma', i', M'}{}' \sum_{\mu', j', N'}{}' G^0_{\sigma\sigma'}(i, M; i', M'; \mathfrak{z}_r) \times M_{\sigma'\mu'}(i', M'; j', N'; \mathfrak{z}_r) G_{\mu'\mu}(j', N'; j, N; \mathfrak{z}_r)\,. \tag{3.4}$$

Thus, in Eq. (3.3) $\underline{G}$, $\underline{G}^0$, and $\underline{M}$ are matrices whose rows and columns are labeled by the trio of indices (σ, i, M), where the Greek index assumes the values 1 and 2, the small Roman index labels the molecule, and the capital Roman index is the magnetic quantum number ± 1. We shall use a matrix notation in which missing indices label rows and columns. Thus, for example, $\underline{G}_{\sigma\sigma'}$ is a matrix in the labels $(i, M; j, N)$ and $\underline{G}_{\sigma\sigma'}(M; N)$ is a matrix in the labels (i, j). The symmetry properties of $\underline{G}$ and $\underline{M}$ are discussed in detail in Appendix C.

The remainder of this subsection is devoted to showing that the usual harmonic results are obtained when the full quadratic Hamiltonian $\mathcal{H}_2$ is treated. In Sec. III B we show that more generally the anharmonic normal-mode frequencies are obtained from a dynamical matrix in which the harmonic force constants are generalized to include anharmonic effects.[76]

Let us discuss the normal-mode problem in this formalism when only the quadratic terms in $\mathcal{H}_2$ are considered. We write

$$\mathcal{H}_2 = \mathcal{H}_{00} + V_2\,, \tag{3.5}$$

and we must calculate the self-energy from all skeleton diagrams[72,73] which can be formed using the interaction V_2, which is represented by vertices of the type shown in Fig. 1. It is clear that for such a quadratic interaction first-order perturbation theory yields an exact evaluation of the self-energy. Thus we have[78,79]

$$M_{11}(i, M; j, N; \mathfrak{z}) = -\zeta^{M,-N}_{ij}\,, \tag{3.6a}$$

$$M_{12}(i, M; j, N; \mathfrak{z}) = \zeta^{M,N}_{ij}\,, \tag{3.6b}$$

as can be seen from Eq. (2.14). From the general symmetry relations Eqs. (C6) and (C11) we have

$$M_{21}(i, M; j, N; \mathfrak{z}) = M_{12}(i, M; j, N; -\mathfrak{z}^*)^*\,, \tag{3.7a}$$

$$M_{22}(i, M; j, N; \mathfrak{z}) = M_{11}(i, M; j, N; -\mathfrak{z}^*)^*\,. \tag{3.7b}$$

It is easily seen from Eq. (3.3) that this form of the self-energy leads to a Green's function with poles. These poles occur at the solutions of

$$\mathrm{Det}\,|(\underline{G}^0)^{-1} - \underline{M}| = 0\,. \tag{3.8}$$

These equations are identical to those [viz., Eq. (22) of Ref. 49] for the harmonic normal-mode frequencies. Thus by taking account of V_2 exactly, we reproduce the previous results for the unperturbed libron spectrum.[45-49] The details of the treatment of the normal-mode problem within the present formalism are given in Appendix A.

B. Anharmonic Dynamical Matrix

The formalism of Sec. III A provides a systematic framework within which anharmonic effects can be discussed. To do this it is clear that we should evaluate contributions to the self-energy from the higher-order anharmonic interactions V_3, V_4, etc. As we have already noted, this program leads to an expansion in powers of $1/z$. Accordingly, we shall evaluate the self-energy to one order higher in $1/z$ than harmonic theory, Eqs. (3.6) and (3.7).

In conformity with the discussion following Eq. (2.19), we consider the matrix elements of the self-energy in Eqs. (3.6) and (3.7) to be $O(1)$, since they do not involve any sums over nearest neighbors or any energy denominators. We note that the diagonal matrix elements in Eq. (3.8) are of order z, since they involve the molecular field energy E_0. Accordingly, we shall evaluate the diagonal matrix elements, e.g., $M_{\sigma\sigma'}(i, M; i, M'; \mathfrak{z})$, etc. to

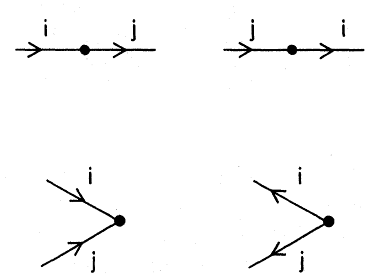

FIG. 1. Diagrammatic representation of the quadratic perturbations V_2. Exact treatment of these interactions yields the usual linear theory of librons.

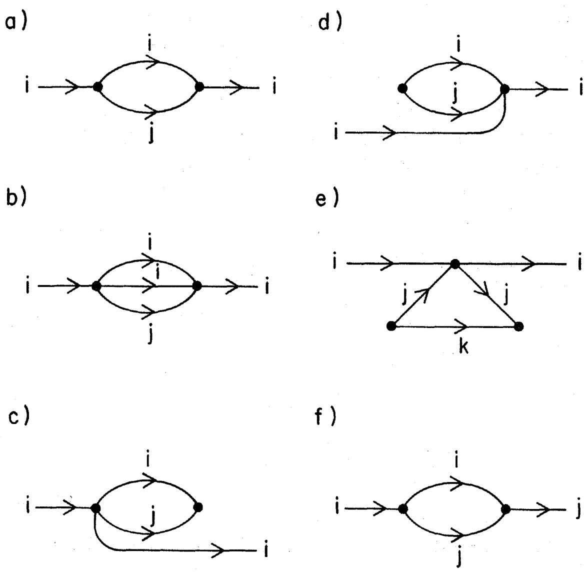

FIG. 2. Diagrams which contribute to $\underline{M}_{11}(i;\ j)$. To reduce the number of diagrams we have not explicitly labeled the lines according to whether they represent $M=+1$ or $M=-1$ propagators. There are no momentum labels on the propagators, because the unperturbed Hamiltonian describes localized excitations.

order 1, and the off-diagonal matrix elements $M_{\sigma\sigma'}(i, M; j, M'; \mathcal{E})$, $i\neq j$, etc., to order $1/z$. In this way we shall evaluate all corrections to the harmonic dynamical matrix which are of relative order $1/z$.

In Figs. 2 and 3 we show the diagrams which contribute to $\underline{M}_{11}(\mathcal{E})$ and $\underline{M}_{12}(\mathcal{E})$ in the desired order in $1/z$. Roughly speaking each energy denominator is of order $1/z$ and each interaction is of order unity. An exception to this statement is provided by the diagram in Fig. 2(e). Here we have two energy denominators, but also two independent lattice sums, so that the contribution is of order unity.

Specifically, the contribution C to $M_{11}(i, M; i, M; \mathcal{E})$ for the diagram of Fig. 2(e) is

$$C=\tfrac{1}{4}\,\mathcal{E}_0^{-2}\sum_{\substack{j,k\\ M',N}}{}' \zeta_{ij}^{0,0}\,|\zeta_{ij}^{M',N}|^2\,, \tag{3.9}$$

where $\mathcal{E}_0$ is the single-libron energy for which we can use either E_0 or E_L [see Eq. (3.21) below]. We note that $E_0=-\frac{2}{3}\sum_k \zeta_{ik}^{0,0}$ and since $E_0\approx\mathcal{E}_0$, we may write Eq. (3.9) as

$$C=-(3/4)z_0^{-1}\sum_l\left(|\zeta_{kl}^{1,1}|^2+|\zeta_{kl}^{1,-1}|^2\right)\,. \tag{3.10}$$

Written in this form, it is clear that C is of the same order as the terms from the other diagrams of Fig. 2. Further insight into this grouping of diagrams according to powers of $1/z$ is obtained by considering the diagrams in Fig. 4, which we have neglected as being of higher order in this parameter. For instance, in Fig. 4(a) we show a typical

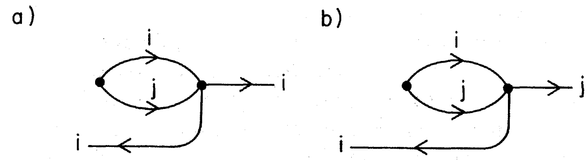

FIG. 3. Diagrams which contribute to $\underline{M}_{12}(i;\ j)$.

contribution involving V_6. Here we clearly have two energy denominators and one lattice sum, hence obtaining a result of order $1/z$, which is one order higher in $1/z$ than is obtained from the diagrams of Figs. 2(a)–2(e). We have also not kept the diagram of Fig. 4(b) analogous to that of Fig. 2(e) for $\underline{M}_{11}(i, j; \mathcal{E}_r)$. This diagram has two energy denominators and a lattice sum over $\vec{R}_k$. As a result, one might be tempted to classify it as being of order $1/z$ and hence comparable to that in Fig. 2(e), which we have kept. However, note that in Fig. 4(b) $\vec{R}_k$ must be a nearest neighbor of both $\vec{R}_i$ and $\vec{R}_j$ (remember that we treat only the anharmonic effects of nearest-neighbor interactions), whereas in Fig. 2(e) the sum over $\vec{R}_k$ is over all nearest neighbors of $\vec{R}_j$. The former are clearly less numerous than the latter in the ratio 4:12. Form this we conclude that the expansion parameter is not simply $1/z$, but is really related to the number of successively longer random walks on the lattice.

By starting from the molecular field Hamiltonian

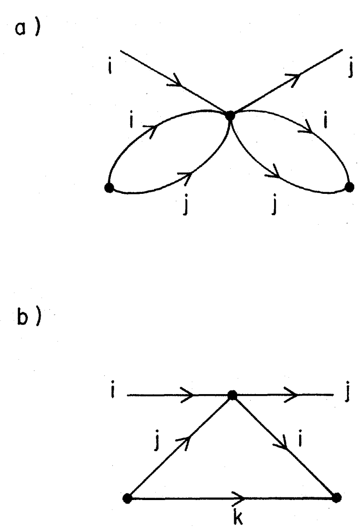

FIG. 4. Diagrams which are neglected as being of higher order in $1/z$ than those of Fig. 2. Diagram (a) has one more energy denominators and hence gives a contribution smaller by order $1/z$ than diagram (e) of Fig. 2. Diagram (b) has two energy denominators and one lattice sum. The lattice sum is not proportional to z since the site k must be a nearest neighbor of both i and j. Hence this term is of higher order in $1/z$ than that of diagram (e) of Fig. 2.

we avoid the necessity of expressing the anharmonic interactions in terms of the normal modes. In our formalism the diagonalization can be performed after the perturbation-theory evaluation of the self-energy. For this reason it is perhaps physically most revealing to present our results in the form of an effective quadratic Hamiltonian $\mathcal{H}_{\text{eff}}$ which is an energy-dependent Hamiltonian defined by the requirement that it lead to the correct self-energy. (This formulation is not rigorous. A more precise discussion is given in Appendix A.) Thus we write

$$\mathcal{H}_{\text{eff}} = E_0 \sum_{i,M}{}' c^\dagger_{iM} c_{iM} + \sum_{i,M,j,N}{}' M_{11}(i, M; j, N) c^\dagger_{iM} c_{jN} + \frac{1}{2} \sum_{i,M,j,N}{}' [M_{12}(i, M; j, N) c^\dagger_{iM} c^\dagger_{jN} + M_{12}(i, M; j, N)^* c_{iM} c_{jN}] \tag{3.11}$$

and we set

$$\underline{M} = \underline{M}^0 + \delta\,\underline{M}\ , \tag{3.12}$$

where $\underline{M}^0$ is the value of the self-energy matrix in the harmonic approximation and $\delta\,\underline{M}$ includes the effects of anharmonicity. As our arguments imply, $\delta\,\underline{M}$ is of relative order $1/z$ compared to $\underline{M}^0$. Thus

$$M^0_{11}(i, M; j, N) = -\zeta^{M,-N}_{ij}\ , \tag{3.13a}$$

$$M^0_{12}(i, M; j, N) = \zeta^{M,N}_{ij}\ . \tag{3.13b}$$

From the diagrams of Figs. 2 and 3 we obtain

$$\delta M_{11}(i, M; j, N) = \tfrac{1}{2}\delta_{ij}\delta_{MN}(\mathcal{E} - 2\mathcal{E}_0)^{-1} \sum_{\substack{k\\ M', M'', N'}}{}' |\zeta^{M'-M'', N'}_{ik}|^2 + \delta_{ij}\delta_{MN}[\tfrac{3}{2}(\mathcal{E} - 3\mathcal{E}_0)^{-1} + \tfrac{9}{4}(2\mathcal{E}_0)^{-1}] \sum_{\substack{k\\ M', N'}}{}' |\zeta^{M', N'}_{ik}|^2$$
$$+ (\mathcal{E} - \mathcal{E}_0)^{-1} \sum_{M', N'}{}' \zeta^{M'-M, N'*}_{ij} \zeta^{M', N'-N}_{ij} \tag{3.14a}$$

and

$$\delta M_{12}(i, M; j, N) = \delta_{ij}\delta_{M,-N}(-2\mathcal{E}_0)^{-1} \sum_{\substack{k\\ M', N'}}{}' |\zeta^{M', N'}_{ik}|^2$$
$$+ (-2\mathcal{E}_0)^{-1} \sum_{M', N'}{}' \zeta^{M-M', N-N'}_{ij} \zeta^{M', N'}_{ij}\ . \tag{3.14b}$$

Here $\mathcal{E}_0$ is the average single-libron energy. It can either be set equal to E_0 or, preferably, be determined self-consistently. Comparison of Eqs. (3.13) and (3.14) shows that the perturbative terms are indeed corrections which are one order higher in the parameter $1/z$.

The remainder of the calculation is now formally identical to the harmonic theory, except that the harmonic dynamical matrix (viz., $\underline{M}^0$) has been replaced by a dynamical matrix (viz., $\underline{M}$) which includes anharmonic effects. Since the calculations are algebraically complicated, we shall present the details in Appendix A and shall outline the procedure in more general terms here. These anharmonic libron energies are found as the roots of Eq. (3.8). Since crystal momentum is conserved, one introduces spatial Fourier transforms in which the position label is replaced by a momentum and a sublattice label. Then $\underline{G}$, $\underline{G}^0$, and $\underline{M}$ are (16×16) momentum-dependent matrices in the subscripts (α, σ, M), where α labels the sublattice and σ and M are as above. The first part of Appendix A [see Eqs. (A7) and (A8)] is devoted to relating $\underline{M}$ in this representation to the results of this section, e.g., Eq. (3.14). The harmonic Green's functions obtained when $\underline{M}$ is given by Eqs. (3.6) and (3.7) are constructed [see Eq. (A29)] and yield the usual harmonic libron spectrum. In the general anharmonic case, the secular equation (3.8) is studied in the momentum representation and it is shown that the anharmonic libron energies may be obtained from an (8×8) matrix as in Eq. (A24). Explicit anharmonic calculations are confined to the case of zero wave vector when a group-theoretical reduction of the dynamical matrix into one- and two-dimensional diagonal blocks corresponding to the irreducible representations E_g and T_g, respectively, is performed. The secular equation for the doubly degenerate E_g mode within the approximation of Eq. (3.14) is given explicitly in Eq. (A47). The secular equation for the two triply degenerate T_g modes may be obtained from Eq. (A40) in terms of (2×2) matrices which are defined explicitly in Eqs. (A41) and (A46). Calculations of the anharmonic libron frequencies throughout the Brillouin zone are in progress and will be reported later.

IV. RESULTS

A. Average Libron Energy

In order to get a feeling for the size of the anharmonicity we first study the libron energy averaged over all modes and over all momenta in the Brillouin zone which we denote by E_L. In practice the easiest way to evaluate E_L is to treat Eq. (3.11) using perturbation theory, taking the molecular field term $E_0 \sum'_{iM} c^\dagger_{iM} c_{iM}$ to be the unperturbed Hamiltonian. Then it follows that

$$E_L = E_0 + \delta M_{11}(i, M; i, M) - (2\mathcal{E}_0)^{-1} \sum_{j,N}{}' |M_{12}(i, M; j, N)|^2 \quad (4.1a)$$

$$= E_0 + \delta M_{11}(i, M; i, M) - (2\mathcal{E}_0)^{-1} \sum_{j,N}{}' |M^0_{12}(i, M; j, N)|^2 . \quad (4.1b)$$

In going from Eq. (4.1a) to (4.1b) we have dropped the terms in (δM_{12}) as being of higher order in $1/z$. We write this as[80]

$$E_L = E_0 + \Delta E^{(2)} + \Delta E^{(3\text{-}3)} + \Delta E^{(2\text{-}4)} + \Delta E^{(4\text{-}2)} + \Delta E^{(2\text{-}4\text{-}2)} + \Delta E^{(4\text{-}4)} , \quad (4.2)$$

where $\Delta E^{(2)}$ represents the effect of the harmonic terms V_2 on the average libron energy and is given as[49]

$$\Delta E^{(2)} = -(2\mathcal{E}_0)^{-1} \sum_{j,N}{}' |M^0_{12}(i, M; j, N)|^2 \quad (4.3a)$$

$$= -(2\mathcal{E}_0)^{-1} \sum_j (|\zeta^{1,-1}_{ij}|^2 + |\zeta^{1,1}_{ij}|^2) . \quad (4.3b)$$

The superscripts on the other terms in Eq. (4.2) indicate the V_n involved. Thus $\Delta E^{(3\text{-}3)}$ is the contribution from the diagram of Fig. 2(a) involving two V_3 (cubic) interactions:

$$\Delta E^{(3-3)} = -\tfrac{1}{2}(2\mathcal{E}_0 - z)^{-1} \sum_{j, M, M', N}{}' |\zeta^{M-M',N}_{2j}|^2 . \quad (4.3c)$$

The other terms in Eq. (4.2) come from the diagrams of Figs. 2(c), 2(d), 2(e), and 2(b), respectively, and are

$$\Delta E^{(2\text{-}4)} = \Delta E^{(4\text{-}2)} = \frac{3}{4\mathcal{E}_0} \sum_{j, M, N}{}' |\zeta^{M,N}_{ij}|^2 , \quad (4.3d)$$

$$\Delta E^{(2\text{-}4\text{-}2)} = -\frac{3}{8\mathcal{E}_0} \sum_{j, M, N}{}' |\zeta^{M,N}_{ij}|^2 , \quad (4.3e)$$

$$\Delta E^{(4\text{-}4)} = \tfrac{3}{2}(3\mathcal{E}_0 - \mathcal{E})^{-1} \sum_{j, M, N}{}' |\zeta^{M,N}_{ij}|^2 . \quad (4.3f)$$

The results of Eq. (4.3) differ from those given previously in Eq. (68) of Ref. 49 where we incorrectly did not include the term of Eq. (4.3e) from Fig. 2(e). In addition, we previously did not include further-neighbor interactions in E_0. In Table II we give the numerical evaluation of these terms within various approximations. In the best approximation, both $\mathcal{E}$ and $\mathcal{E}_0$ are evaluated self-consistently, i.e., we set $\mathcal{E} = \mathcal{E}_0 = E_L$, which yields

$$E_L = 16.13\Gamma . \quad (4.4)$$

Other approximations are generated by using a self-energy in which either or both $\mathcal{E}$ and $\mathcal{E}_0$ are set equal to E_0 rather than to E_L. Note that in all the approximations studied, the cubic terms are by far the most important. Thus, completely neglecting the other terms gives very good results, as we have shown in the table.

B. Libron Energies at $k=0$

We have evaluated the libron energies at zero wave vector. For the E_g mode the anharmonic secular equation is given explictly by Eq. (A47). For the T_g modes the secular equation was constructed and solved numerically in accordance with the formulation in Appendix A. The results of these calculations for zero wave vector are compared with the results of harmonic theory in Table III. A striking feature of these results is that the highest-energy mode is strongly shifted to lower energy by the anharmonic perturbation. This result is explained by the familiar "repulsion of energy levels" in perturbation theory. The highest-energy libron mode is the one closest to the two-libron modes (to which the large cubic anharmonicity couples) and hence has the smallest energy denominator. In addition the matrix element coupling this mode to the two-libron modes is also larger than that for the other modes. These results differ slightly from those quoted previously[11] where we used the value of $\mathcal{E}_0$ obtained using Rayleigh-Schrödinger perturbation theory, $\mathcal{E}_0 = 17\Gamma$, rather than the fully self-consistent libron energy, $\mathcal{E}_0 = 16.13\Gamma$, as we do here. For comparison, we also include in Table III results obtained using Rayleigh-Schrödinger and Brillouin-Wigner perturbation theory.

We conclude this subsection by making some comments on the form of our results. We note that the energy denominators in Eq. (3.14) involve the molecular field energy, since $\mathcal{E}_0 \approx E_0$. We could

TABLE II. Contributions to the average libron energy E_L within different approximations.

Term	Self-consistent $\mathcal{E} = \mathcal{E}_0 = E_L$	Rayleigh-Schrödinger[a] $\mathcal{E} = \mathcal{E}_0 = E_0$	Brillouin-Wigner $\mathcal{E} = E_L$; $\mathcal{E}_0 = E_0$
$\Delta E^{(2)}$	-0.37[b]	-0.28[b]	-0.28[b]
$\Delta E^{(3\text{-}3)}$	-5.26	-4.00	-3.47
$\Delta E^{(4\text{-}2)}$	1.11	0.84	0.84
$\Delta E^{(2\text{-}4)}$	1.11	0.84	0.84
$\Delta E^{(2\text{-}4\text{-}2)}$	-0.55	-0.42	-0.42
$\Delta E^{(4\text{-}4)}$	-1.11	-0.84	-0.78
E_L	16.13	17.34	17.93
$E_0 + \Delta E^{(3\text{-}3)}$	15.94	17.20	17.73

[a]The results of Ref. 49 were evaluated for $\mathcal{E} = \mathcal{E}_0 = 19\Gamma$, as is true for nearest-neighbor interactions. Here we include further-neighbor interactions, so that $E_0 = 21.2\Gamma$.

[b]All energies are given as multiples of Γ.

TABLE III. Libron energies at zero wave vector.

Approximation	E_g	T_g	T_g
Harmonic nearest neighbor[a]	10.38[b]	14.32[b]	26.19[b]
Harmonic all neighbor[c]	13.66	17.72	29.04
Anharmonic Rayleigh-Schrödinger[d] $\mathfrak{z}=\mathfrak{z}_0=E_0=21.2\Gamma$	11.62	14.97	23.04
Anharmonic Brillouin-Wigner $\mathfrak{z}_0=E_0=21.2\Gamma$	12.10	15.45	22.75
Anharmonic self-consistent $\mathfrak{z}_0=16.13\Gamma_0$	11.29	14.07	19.55

[a]See Refs. 45–47.
[b]All energies are given as multiples of Γ.
[c]See Refs. 48–50.
[d]In other words, the libron energies are determined as the eigenvalues of the dynamical matrix evaluated at $\mathfrak{z}=E_0$.

arrive at such a result by alternative reasoning. Suppose we expressed the interaction in terms of normal modes. We would then obtain results similar to those in Eq. (3.14), except that the energy denominator would involve momentum-dependent libron energies. Insofar as these energy denominators can be replaced by E_0, the sums over intermediate states can be done by closure and our results will follow. It is easily seen that such an approximation will be valid providing the spread in libron energies, or bandwidth, is small compared to their average energy. A measure of the bandwidth is given by B, where

$$B^2=(8N_0)^{-1}\sum_{u,\vec{k}}[\omega_\mu(\vec{k})]^2-\left((8N_0)^{-1}\sum_{u,\vec{k}}\omega_\mu(\vec{k})\right)^2 , \tag{4.5}$$

where $\omega_\mu(\vec{k})$ is the libron energy for wave vector $\vec{k}$ and mode index μ, $\mu=1,\ldots,8$. From our previous work[49] we have

$$(B/E_0)^2\approx 1.0-(0.9935)^2\ll 1 , \tag{4.6}$$

which gives an alternative justification of our results. In other words, the effects of finite bandwidth are higher order in $1/z$.

In view of the large shifts in the single-libron energies one might wonder if higher-order effects are important. While we do not pretend to be able to answer this question definitively, it seems to us that such effects are less important, although they may not be negligible. We base this conclusion on the identification of $1/z$ as the expansion parameter. A more conservative estimate of the accuracy of our calculations is obtained by assuming that since we find a 30% shift in the highest-energy libron mode in lowest-order perturbation theory, a second-order calculation would give fractional shifts of order $(0.3)^2\approx(0.1)$. This argument would suggest that the two lower energies are accurate to within 5% and the upper one to within 10%.

C. Raman Intensities

We may evaluate the Raman intensities within this formalism. To do this it is necessary to relate the Raman intensities to a correlation function[81] in much the same way as has been done for the cross section for inelastic scattering of neutrons by crystals.[82] In Appendix B we thereby express the Raman intensities in terms of the Green's functions. In this way we have included anharmonic effects in the calculations of the Raman intensities. The results of these calculations are shown in Table IV. They differ from those given in Ref. 11, where the intensities were calculated using the harmonic formulas, but inserting the anharmonic frequencies. That type of approximation does not reflect strongly enough the alteration in intensity which inevitably accompanies perturbative frequency shifts.[83]

It should be noted that such a calculation gives nonvanishing intensity from two-libron processes. These resonances are reflected by the appearance of poles in the self-energy for $\hbar\omega=2E_0$. To simplify the discussion let us consider a single-particle Green's function of the form

$$G=\left(\mathfrak{z}-E_0-\frac{|V|^2}{\mathfrak{z}-2E_0}\right)^{-1} . \tag{4.7}$$

A spectral resolution yields

$$G=\frac{A_1}{\mathfrak{z}-E_1}+\frac{A_2}{\mathfrak{z}-E_2} \tag{4.8}$$

TABLE IV. Intensities calculated within various approximations.

Approximation	E_g	$T_g^{(-)}$ [a]	$T_g^{(+)}$ [a]
Harmonic nearest neighbors[b]	4.88[c]	1.46[c]	0.17[c]
Harmonic all neighbors[d]	4.14	1.31	0.17
Anharmonic Rayleigh-Schrödinger	4.32	1.10	0.31
Anharmonic Brillouin-Wigner	4.15	1.05	0.27
Anharmonic self-consistent	3.98	0.84	0.32

[a]Here $T_g^{(-)}$ ($T_g^{(+)}$) is the lower- (higher-) energy T_g mode.
[b]See Ref. 49.
[c]Here we quote W/C_0 as calculated from Eq. (B19).
[d]See Refs. 49 and 50.

with $A\approx 1$, $E_1\approx E_0$, $A_2\approx |V|^2/E_0^2$, and $E_2\approx 2E_0$, assuming $|V|/E_0\ll 1$. The interpretation of this result is clear: In addition to single-particle excitations, there are weaker two-particle excitations. Thus the poles in the self-energy at $2E_0$ reflect the existence of the two-libron states whose energies are calculated in the accompanying paper.[12] A similar argument shows that there will be resonances involving three or more librons at even higher overtones, but these will be broader and weaker in intensity.

Interesting information about the two-libron modes can also be obtained through the use of sum rules which the correlation functions must satisfy. In this respect the theory of libron waves is formally identical to that of phonons.[84] It is clear from the work in Appendix B [see Eqs. (B5)–(B7)] that the frequency dependence of the Raman intensity, $W(\omega)$, is given by the spectral weights of a linear combination of Green's functions. Let us denote this linear combination of Green's functions by $H(\mathfrak{z})$. Thus we have

$$W(\omega)=2C_0(1-e^{-\beta\omega})^{-1}(2\pi i)^{-1}[H(\omega-i0^+)-H(\omega+i0^+)]\,, \tag{4.9}$$

where C_0 is a constant. Then, by dispersion theory we may write

$$H(\mathfrak{z})=(2C_0)^{-1}\int_{-\infty}^{+\infty}\frac{W(\omega)}{\mathfrak{z}-\omega}(1-e^{-\beta\omega})d\omega\,. \tag{4.10}$$

In Appendix D it is shown that $H(\mathfrak{z})$ is an even function of $\mathfrak{z}$ and therefore that $W(\omega)(1-e^{-\beta\omega})$ must be an odd function of ω. Thus for large $\mathfrak{z}$ we have an asymptotic expansion of the form

$$H(\mathfrak{z})\sim M_1\mathfrak{z}^{-2}+M_3\mathfrak{z}^{-4}+\cdots\,, \tag{4.11}$$

where

$$M_1=(2C_0)^{-1}\int_{-\infty}^{+\infty}W(\omega)(1-e^{-\beta\omega})\omega\,d\omega \tag{4.12a}$$

$$=C_0^{-1}\int_0^{\infty}W(\omega)(1-e^{-\beta\omega})\omega\,d\omega \tag{4.12b}$$

$$=C_0^{-1}\int_0^{\infty}\omega W(\omega)\,d\omega,\qquad T\to 0 \tag{4.12c}$$

and likewise

$$M_3=C_0^{-1}\int_0^{\infty}W(\omega)(1-e^{-\beta\omega})\omega^3\,d\omega \tag{4.13a}$$

$$=C_0^{-1}\int_0^{\infty}\omega^3 W(\omega)\,d\omega\,,\quad T\to 0\,. \tag{4.13b}$$

Thus we see that the coefficients in the large-$\mathfrak{z}$ expansion of $H(\mathfrak{z})$ are related to the frequency moments of the Raman spectrum.

We can exploit these relations in various ways. For the harmonic calculations, they provide an exact check on our analytic and numerical work, because within this approximation all the intensity occurs at the single-libron frequencies. In fact, these sum rules can be applied separetely to excitations of each symmetry. Expressions for the coefficients M_1 and M_2 are derived in Appendix D in terms of our approximate self-energies. In Table V we compare the evaluation of M_1 as calculated in Appendix B for the E_g and T_g modes with the corresponding values of the frequency moments taken over the calculated single-libron spectrum. As we have mentioned, the two results should agree exactly in the harmonic approximation. In the anharmonic calculations we cannot expect to satisfy these sum rules exactly, because the calculated frequency moments do not include the two-libron modes. In fact we can obtain an estimate of the intensity of these processes by assuming that all the weight in the multiple-libron Raman spectrum is concentrated at the two-libron energy, which we take for this calculation to be $2E_L\approx 30\Gamma$. The results we obtain are shown in Table V. Note that the two-libron intensity we estimate in this way is in reasonable agreement with the total intensity of the two-libron spectrum as calculated in the accompanying paper.[12]

Note added in proof. Shortly after this paper was submitted more refined observations of the Raman spectrum of solid H_2 and D_2 were reported by W. N. Hardy, I. F. Silvera, and J. P. McTague, Phys. Rev. Letters 26, 127 (1971). There it was

TABLE V. Sum-rule check on the calculated Raman intensities.

Symmetry	Energy[a] (ω)	Intensity[b] (I)	$I\omega$[c]	M_1[d]	Two-libron intensity[e]
		Harmonic, nearest neighbors			
E_g	10.38	4.88	50.65	50.67	0.0
T_g	14.32 26.19	1.45 0.17	20.91 4.45	25.33	0.0
		Harmonic, all neighbors			
E_g	13.66	4.14	56.55	56.53	0.0
T_g	17.72 29.04	1.31 0.17	23.21 4.94	28.26	0.0
		Anharmonic, Rayleigh-Schrödinger			
E_g	11.62	4.32	50.20	50.20	0.0
T_g	14.97 23.04	1.10 0.31	16.46 7.14	23.52	0.0
		Anharmonic, Brillouin-Wigner			
E_g	12.10	4.15	50.22	61.47	0.37
T_g	15.45 22.75	1.05 0.27	16.22 6.05	29.28	0.23
		Anharmonic, self-consistent			
E_g	11.29	3.98	44.93	63.02	0.60
T_g	14.07 19.55	0.84 0.32	11.82 6.26	29.59	0.38

[a]In units of Γ.
[b]We tabulate W/C_0 as evaluated from Eq. (B19).
[c]Here $I\omega$ denotes intensity times energy.
[d]Evaluated from Eq. (D8) or (D12a) as is appropriate.
[e]Calculated assuming all the missing weight $(M_1-I\omega)$ to be concentrated at the two-libron energy at $\sim 30\Gamma$.

TABLE VI. Comparison of the observed and calculated Raman spectra. All energies are given in cm^{-1} and the relative intensities are given in parentheses. Here Γ_{eff} denotes an effective value of Γ which must be corrected to allow for the presence of a small amount of $(J=0)$ impurity in the sample. As a result the values of Γ deduced from the Raman spectra are about 6% larger than Γ_{eff}. The estimated limits of error in the anharmonic calculations are indicated.

Anharmonic theory (self-consistent)	Observed (see Refs. 42 and 43)	Harmonic theory (all neighbors)
	H_2	
$\Gamma_{eff}=0.56\ cm^{-1}$		$\Gamma_{eff}=0.44\ cm^{-1}$
6.3±0.3 (1.00)	6.2±1 (1.00)	6.2 (1.00)
7.9±0.4 (0.20)	8.0±1 (0.18)	8.0 (0.32)
10.9±1.0 (0.12)	11.3±1 (0.05)	13.0 (0.04)
16.2[a] (0.29)[a]	16.8±1	None
20.5[a] (0.06)[a]	21.0±2	None
	D_2	
$\Gamma_{eff}=0.78\ cm^{-1}$		$\Gamma_{eff}=0.64\ cm^{-1}$
8.8±0.3 (1.00)	8.8±1 (1.00)	8.8 (1.00)
11.0±0.5 (0.20)	11.2±1 (0.34)	11.3 (0.32)
15.2±1.5 (0.12)	15.1±1 (0.12)	18.6 (0.04)
22.6[a] (0.29)[a]	22.5±1 (0.20)	None
28.5[a] (0.06)[a]	29.9±2 (0.04)	None

[a]See Ref. 12.

pointed out that the polarization dependence of the intensity of the single-libron modes depends only on their symmetry. It was found that the experimental intensities for various polarizations agreed extremely well with the group theoretical predictions. The same reasoning can also be applied to the two-libron modes, since they are also contained in the single-libron spectral weight function. Accordingly, we have used the theoretical polarization dependence of the Raman intensities associated with E_g and T_g modes as given by Hardy *et al.* to determine the symmetry of the two-libron processes. Thus by assuming relative fractions x and $1-x$ of E_g and T_g symmetry for the two-libron process we determined x by a least-squares fit to the observed polarization dependence of the two-libron intensity. The resulting value $x=0.61$ is in close agreement with that predicted in Table V using sum rules. The two-libron intensity for a powder can also be deduced from the data of Hardy *et al.* and is found to be about 20% of the most intense single-libron line, in fair agreement with the calculations of this and the accompanying paper.

V. DISCUSSION AND CONCLUSION

A. Comparison with Experiment

As we have seen, the inclusion of anharmonicity reduces the libron energies, especially that of the highest-energy mode. In addition, the anharmonicity is responsible for the appearance of two-libron processes in the Raman spectrum. In Table VI we compare the calculations of Sec. IV for the single-libron energies and those of the accompanying paper for the two-libron energies with the observed Raman spectrum. A similar comparison with the harmonic calculations is also given. It is clear that the large downward shift of the highest-energy single-libron mode is needed to bring theory and experiment into agreement. From this table it is seen that the agreement between theory and experiment is closer for the frequencies than for the intensities. Nevertheless, the fit is excellent and the effects of anharmonic libron-libron interactions are strikingly confirmed. A graphical comparison of the theoretical and experimental Raman spectra is shown in Figs. 3 and 4 of the accompanying paper.[12]

Actually, the above analysis does not take account of the fact that the experiments were performed, not on pure $(J=1)$ solids, but on alloys containing about 3% of the $(J=0)$ species as an impurity. As a result Γ is somewhat larger than the effective value of Γ, denoted Γ_{eff}, used to fit the Raman data. However, since the theory of excitations in multisublattice alloys has not been established, we shall rely on the experimental data of Ramm *et al.*[23] to extrapolate the experimental results to the pure $(J=1)$ solid.[85] By measuring $(\partial p/\partial T)_V$ (a quantity which is essentially equivalent to the specific heat) they showed that the average libron energy E_L depends on the concentration of $(J=1)$ molecules, x, as[23]

$$E_L(x)/k_B=(38.9x-19.0)\,\mathrm{K} \tag{5.1}$$

for x near unity. Since the Raman work was done on samples with $x\approx 0.97$, this relation implies that $\Gamma/\Gamma_{eff}=1.06$. Thus the fit in Table VI yields

$$\Gamma=0.59\ \mathrm{cm}^{-1}\ \text{ for } H_2\,, \tag{5.2a}$$

$$\Gamma=0.83\ \mathrm{cm}^{-1}\ \text{ for } D_2\,. \tag{5.2b}$$

The anharmonic corrections found here also influence the analysis of other experiments. For instance, Ramm *et al.*[23] have analyzed the libron specific heat as determined both directly[20] and indirectly via their $(\partial p/\partial T)_V$ measurements in terms of the harmonic density of states calculated by Mertens *et al.*[47] In the absence of a calculation of the anharmonic density of states we assume that the effect of libron-libron interactions is merely to rescale all the libron energies by the same ratio as they do E_L. Then we identify the value of E_L for the pure $(J=1)$ solid,[23]

$$E_L/k_B=19.9\ \mathrm{K}\,, \tag{5.3}$$

with Eq. (4.4) and obtain[86]

$$\Gamma=0.79\ \mathrm{cm}^{-1}\,. \tag{5.4}$$

This value of Γ is about 25% larger than would be obtained using the harmonic theory (including all-neighbor interactions). Finally, we remark that the anharmonicity does not drastically change the ground-state energy,[50] and consequently, the determination of Γ from the zero-temperature extrapolation of the pressure[22] due to EQQ interactions is not grossly affected by anharmonicity.

In Table VII[87–93] we give a summary of the available determinations of Γ for both D_2 and H_2. We note that most of the methods are quite consistent, except that the low-concentration T_1 data[37,39,40] give anomalous values of Γ, probably indicating that the theory[28,36] is inadequate. From the values Γ given in this table we see that there is no longer any evidence to support the suggestion[64] that the phonon-renormalized value of Γ is smaller at high ($J=1$) concentration than at low ($J=1$) concentration. It also appears that the phonon renormalization is less important in D_2 than in H_2. This result is certainly plausible, but was not indicated by the rough calculations in Ref. 64.

TABLE VII. Experimental values of Γ.

$\Gamma_{expt}{}^{a}/\Gamma_0$	Method	References
	Solid H_2: $\Gamma_0=0.698\ cm^{-1}$ [b]	
0.82 ± 0.04[c]	NMR of isolated ($J=1$) pairs	17
0.81 ± 0.02	Raman spectrum of isolated ($J=1$) pairs	87
0.82 ± 0.05	$(\partial p/\partial T)_V$ for $x<0.07$	22
0.90 ± 0.10	Specific heat for $x=0.0022$	88
0.79 ± 0.04	Neutron scattering for $x=0.27$	18, 89, 62
0.60 ± 0.06	NMR, T_1 for $x<0.10$	37, 36, 28
0.82 ± 0.04	Ortho-para pressure difference, $T=0$ K	22, 90
0.75 ± 0.04	Neutron scattering for $x=0.68$, 0.74	18, 16, 89, 62
0.84 ± 0.05	Raman spectrum, $x=0.97$, $T=1.5$ K	42, 43, d
0.81 ± 0.04	NMR, T_1 for $T>5$ K	38, 32, 28, 41
0.80 ± 0.10	Specific heat for $T>5$ K	19, 21
0.87[e]±0.10	Vapor pressure of ortho-para solids	62, 91, 92
	Solid D_2: $\Gamma_0=0.839\ cm^{-1}$ [f]	
0.88 ± 0.06	$(\partial p/\partial T)_V$ for $x<0.07$	23
0.82 ± 0.02	Raman spectrum of isolated ($J=1$) pairs	87
0.60 ± 0.10	NMR, T_1 for $x<0.10$	39, 40, 36, 32
0.99 ± 0.06	Raman spectrum, $x=0.97$, $T=1.5$ K	42, 43, d
0.95 ± 0.04	$(\partial p/\partial T)_V$ for $x>0.83$, $T<2$ K	23, d
0.83 ± 0.08	Specific heat for $T>7$ K	20, 21
0.70 ± 0.10	NMR, T_1 for $T>6$ K	39, 40, 32, 33, 41
0.92[e]±0.08	Vapor pressure of ortho-para solids	93, 92

[a]Γ_{expt} denotes the experimentally deduced value of Γ.

[b]We took $R_0=3.755$ Å (see Ref. 66) and $Q=0.4883a_0^2$ (see Ref. 68).

[c]The error ranges indicate the experimental errors and do not reflect uncertainties in the theoretical models.

[d]This work.

[e]For these experiments the interpretations cited took account of the temperature dependence of the lattice constant by properly scaling the EQQ coupling constant: $\Gamma(T)=\Gamma(0)[R_0(T)/R_0(0)]^5$, where $R_0(T)$ is the nearest-neighbor separation at temperature T.

[f]We took $R_0=3.59$ Å (see Refs. 66 and 67) and $Q=0.4873a_0^2$ (see Ref. 68).

B. Conclusion

We may draw several important conclusions from our work.

(i) In agreement with our previous work,[49] we find that the cubic anharmonicity, which is completely ignored in the RPA, is much more important than the quartic anharmonicity. In fact, ignoring the noncubic anharmonic terms is an excellent approximation.

(ii) The anharmonic shifts in the single-libron spectrum are significant, especially for the highest-energy libron mode. The energies of the two lower-energy modes are reduced by about 15% and the highest-energy mode by about 35% due to the cubic anharmonicity.

(iii) The cubic anharmonicity also influences the intensity ratios in the Raman spectrum. Significantly, the relative intensity of the highest-energy single-libron mode is thereby greatly enhanced. Using sum rules we predict that the two-libron intensity is about 20% that of the single-libron processes. In agreement with experiment (see note added in proof) most of the two-libron intensity arises from the spectral weight function for librons of E_g symmetry.

(iv) The present calculations, since they include all corrections of relative order $1/z$, where z is the number of nearest neighbors, are expected to be qualitatively correct.

(v) The values of Γ deduced by fitting (a) the Raman spectrum or (b) $(\partial p/\partial T)_V$ and specific-heat data to the calculations of the libron spectrum are increased by, respectively, 15 and 25% owing to anharmonicity. Apparently the phonon renormalizations are much less important than previously supposed, especially for D_2.

Several fruitful lines of future investigation are clear. First of all, calculations of the anharmonic libron frequencies should be calculated throughout the entire Brillouin zone. This work is currently in progress and will be reported later. It will be extremely interesting to compare such calculations with determinations of the libron spectrum via inelastic scattering of neutrons. Such experiments would also enable us to place a bound on the size of the non-EQQ-interactions, which are usually assumed to be negligible. In addition, with the advance of experimental techniques it is quite possible that calculation of the energy widths of the single libron-modes will prove useful.

ACKNOWLEDGMENTS

The authors gratefully acknowledge stimulating discussions and advice from Professor H. Meyer. They would like to thank Mr. A. J. Berlinsky for suggesting improvements in notation.

APPENDIX A

Momentum-Sublattice Representation

As is the case with any system with translational periodicity it is convenient to introduce spatial Fourier transforms as a means of facilitating the determination of the normal modes. In such a description one characterizes the quantities of interest, such as the self-energy, by a momentum vector $\vec{k}$ rather than by site indices $\vec{R}_i$ and $\vec{R}_j$. Now since the $Pa3(T_h^6)$ structure consists of a simple-cubic Bravais lattice with four molecules per unit cell, one must specify the position of the molecule within the unit cell in addition to the pseudomomentum $\vec{k}$. The position of a molecule within the unit cell is designated by $\vec{\tau}_\alpha$ and is listed in Table I. We will, for convenience, denote the sublattice by α, with $\alpha = 1, \ldots, 4$.

We introduce operators $c_{\alpha M}(\vec{k})$ which are the Fourier transforms of the operators c_{jM} by the following:

$$c_{\alpha M}(\vec{k}) = N_0^{-1/2} \sum_{j \epsilon \alpha} c_{jM}\, e^{-i\vec{k}\cdot\vec{R}_j} , \tag{A1}$$

where N_0 is the number of unit cells and $\vec{k}$ is a reduced reciprocal-lattice vector lying within the first Brillouin zone. The notation $\sum_{j \epsilon \alpha}$ is taken to indicate that we sum over all sites on a given sublattice α. This is a generalization of the usual Fourier transform and reflects the fact that we are dealing with a space lattice which has a sublattice structure. The Fourier transform of any function of the sites i and j, $V(i, j)$, can be similarly generalized and reads

$$V(\vec{k})_{\alpha\beta} = \sum_{\substack{j \epsilon \beta \\ (i \epsilon \alpha)}} V(i, j) \exp[-i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)] , \tag{A2}$$

where j is summed over the entire βth sublattice, and α and β range from one to four. The notation $(i \epsilon \alpha)$ indicates that i is not summed, but denotes any fixed site in the αth sublattice. Thus, spatial Fourier transforms in the four-sublattice structure can be viewed as (4×4) matrices where the rows and columns of the matrix $V_{\alpha\beta}$ are specified by the sublattice indices α and β, respectively. Likewise we interpret the operators $c_{\alpha M}(\vec{k})$, for given M, as a column vector of four rows.

It is instructive now to rewrite the effective Hamiltonian of Eq. (3.11) in the momentum representation as

$$\mathcal{H}_{\text{eff}} = E_0 \sum_{\vec{k}, \alpha, M}{}' c^\dagger_{\alpha M}(\vec{k}) c_{\alpha M}(\vec{k}) + \sum_{\substack{\vec{k}, \alpha, \beta \\ M, N}}{}' M_{11}(M, N; \vec{k})_{\alpha\beta} c^\dagger_{\alpha M}(\vec{k}) c_{\beta N}(\vec{k})$$
$$+ \frac{1}{2} \sum_{\substack{\vec{k}, \alpha, \beta \\ M, N}}{}' [M_{12}(M, N; \vec{k})_{\alpha\beta} c^\dagger_{\beta N}(\vec{k}) c^\dagger_{\alpha M}(-\vec{k}) + M_{12}(M, N; \vec{k})^*_{\alpha\beta} c_{\alpha M}(\vec{k}) c_{\beta N}(-\vec{k})] , \tag{A3}$$

where, in accordance with our prescription for spatial Fourier transforms,

$$M_{\sigma\sigma'}(M, N; \vec{k})_{\alpha\beta} = \sum_{\substack{j \epsilon \beta \\ (i \epsilon \alpha)}} M_{\sigma\sigma'}(i, M; j, N) \times \exp[-i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)] . \tag{A4}$$

The (8×8) matrices $\underline{M}_{11}$ and $\underline{M}_{12}$ are defined in analogy with Eq. (3.12) as

$$\underline{M}_{11}(\vec{k}) = \underline{M}^0_{11}(\vec{k}) + \underline{\delta M}_{11}(\vec{k}) , \tag{A5a}$$

$$\underline{M}_{12}(\vec{k}) = \underline{M}^0_{12}(\vec{k}) + \underline{\delta M}_{12}(\vec{k}) , \tag{A5b}$$

where $\underline{M}^0_{11}(\vec{k})$ and $\underline{M}^0_{12}(\vec{k})$ are the values of $\underline{M}_{11}(\vec{k})$ and $\underline{M}_{12}(\vec{k})$ in the harmonic approximation:

$$\underline{M}^0_{11}(\vec{k}) = \begin{array}{|c|c|} \hline M^0_{11}(1, 1; \vec{k})_{\alpha\beta} & M^0_{11}(1, -1; \vec{k})_{\alpha\beta} \\ \hline M^0_{11}(-1, 1; \vec{k})_{\alpha\beta} & M^0_{11}(-1, -1; \vec{k})_{\alpha\beta} \\ \hline \end{array} \tag{A6a}$$

and

$$\underline{M}^0_{12}(\vec{k}) = \begin{array}{|c|c|} \hline M^0_{12}(1, 1; \vec{k})_{\alpha\beta} & M^0_{12}(1, -1; \vec{k})_{\alpha\beta} \\ \hline M^0_{12}(-1, 1; \vec{k})_{\alpha\beta} & M^0_{12}(-1, -1; \vec{k})_{\alpha\beta} \\ \hline \end{array} . \tag{A6b}$$

Using Eqs. (3.7) and (A2) we find

$$M^0_{11}(M, N; \vec{k})_{\alpha\beta} = -\sum_{\substack{j \epsilon \beta \\ (i \epsilon \alpha)}} \zeta^{M, -N}_{ij} \exp[-i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)] , \tag{A7a}$$

$$M^0_{12}(M, N; \vec{k})_{\alpha\beta} = \sum_{\substack{j \epsilon \beta \\ (i \epsilon \alpha)}} \zeta^{M, N}_{ij} \exp[-i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)] , \tag{A7b}$$

and within the approximation of Eq. (3.14) we have

$$\delta M_{11}(M,N;\vec{k},\mathfrak{z})_{\alpha\beta}=\delta_{\alpha\beta}\delta_{MN}\Big(\tfrac{1}{2}(\mathfrak{z}-2\mathfrak{z}_0)^{-1}\sum_{\substack{l\\ M',M'',N'}}{}'\,|\zeta_{il}^{M'-M'',N'}|^2+[\tfrac{3}{2}(\mathfrak{z}-3\mathfrak{z}_0)^{-1}+\tfrac{9}{4}(2\mathfrak{z}_0)^{-1}]\sum_{\substack{l\\ M',N'}}{}'\,|\zeta_{il}^{M',N'}|^2\Big)$$
$$+(\mathfrak{z}-2\mathfrak{z}_0)^{-1}\sum_{\substack{j\in\beta\\(i\in\alpha)}}\sum_{M',N'}{}'\exp[-i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)]\,\zeta_{ij}^{M'-M,N'*}\zeta_{ij}^{M',N'-N}\,, \qquad \text{(A8a)}$$

$$\delta M_{12}(M,N;\vec{k},\mathfrak{z})_{\alpha\beta}=\delta_{\alpha\beta}\delta_{M,-N}(-2\mathfrak{z}_0)^{-1}\sum_{\substack{l\\ M',N'}}{}'\,|\zeta_{ij}^{M',N'}|^2+(-2\mathfrak{z}_0)^{-1}\sum_{\substack{j\in\beta\\(i\in\alpha)}}\sum_{M',N'}{}'\exp[-i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)]\,\zeta_{ij}^{M-M',N-N'}\zeta_{ij}^{M',N'}\,. \qquad \text{(A8b)}$$

The following symmetry relations discussed in Appendix C will prove useful later:

$$\underline{M}_{11}(-M,-N;\vec{k},\mathfrak{z})=\underline{M}_{11}(M,N;\vec{k},\mathfrak{z}^*)^*\,, \qquad \text{(A9a)}$$

$$\underline{M}_{12}(-M,-N;\vec{k},\mathfrak{z})=\underline{M}_{12}(M,N;\vec{k},\mathfrak{z}^*)^*\,. \qquad \text{(A9b)}$$

In order to emphasize the physical aspect of our calculations we have described the effects of anharmonic interactions in terms of an effective Hamiltonian, Eq. (A3). In this interpretation the effective Hamiltonian describes a system of harmonic oscillators coupled by frequency-dependent "force constants" which have been renormalized to include the effects of anharmonicity. This formulation is, strictly speaking, not precise since the frequency dependence of such renormalized force constants can not be defined in a completely satisfactory way. In order to discuss the frequency dependence of the effective interaction a more formal calculation is needed. Such a calculation is achieved by constructing the complete self-energy $\underline{M}(\vec{k},\mathfrak{z})$. The components $\underline{M}_{11}(\vec{k},\mathfrak{z})$ and $\underline{M}_{12}(\vec{k},\mathfrak{z})$ have been given in Eqs. (A7) and (A8). The other components of $\underline{M}(\vec{k},\mathfrak{z})$ are determined by the symmetry relations of Appendix C as

$$\underline{M}_{21}(\vec{k},\mathfrak{z})=\underline{M}_{12}(\vec{k},-\mathfrak{z}^*)^*\,, \qquad \text{(A10a)}$$

$$\underline{M}_{22}(\vec{k},\mathfrak{z})=\underline{M}_{11}(\vec{k},-\mathfrak{z}^*)^*\,. \qquad \text{(A10b)}$$

Having constructed the momentum representation for the self-energy we proceed to the solution of the Dyson equation relating the Green's function to the self-energy by first introducing the momentum representation of the Green's functions defined in Eq. (3.1):

$$G_{11}(M,N;\vec{k},t)_{\alpha\beta}=-i\langle c_{\alpha M}(\vec{k},t)c_{\beta N}^{\dagger}(\vec{k})\rangle\,, \qquad \text{(A11a)}$$

$$G_{12}(M,N;\vec{k},t)_{\alpha\beta}=-i\langle c_{\alpha M}(\vec{k},t)c_{\beta N}(-\vec{k})\rangle\,, \qquad \text{(A11b)}$$

$$G_{21}(M,N;\vec{k},t)_{\alpha\beta}=-i\langle c_{\alpha M}^{\dagger}(-\vec{k},t)c_{\beta N}^{\dagger}(\vec{k})\rangle\,, \qquad \text{(A11c)}$$

$$G_{22}(M,N;\vec{k},t)_{\alpha\beta}=-i\langle c_{\alpha M}^{\dagger}(-\vec{k},t)c_{\beta N}(-\vec{k})\rangle\,, \qquad \text{(A11d)}$$

with t in the interval $(0,-i\beta)$.

The temporal Fourier coefficients $G_{\sigma\sigma'}(M,N;k,\mathfrak{z}_r)_{\alpha\beta}$ are defined as in Eq. (3.2).

Solution of Dyson Equation

In order to find the anharmonic normal modes and their associated frequencies we need to solve Eq. (3.4) for $\underline{G}$ in terms of the self-energy $\underline{M}$. In doing so we naturally find that the quasiparticle energies are determined by the condition

$$\mathrm{Re\,Det}\,|(\underline{G}^0)^{-1}-\underline{M}|=0\,. \qquad \text{(A12)}$$

This is a generalization of the usual formula

$$\mathrm{Re}\{\omega-\epsilon_{\vec{k}}-M_{\vec{k}}(\omega)\}=0 \qquad \text{(A13)}$$

and reflects the fact that we deal here with matrix Green's functions.

We can write the Dyson equation in terms of the matrices $\underline{G}_{\sigma\sigma'}$ and $\underline{M}_{\sigma\sigma'}$ as follows:

$$\underline{G}=\begin{vmatrix}\underline{G}_{11} & \underline{G}_{12}\\ \underline{G}_{21} & \underline{G}_{22}\end{vmatrix}=\begin{vmatrix}(\mathfrak{z}-E_0)\underline{I}-\underline{M}_{11}(\vec{k},\mathfrak{z}) & -\underline{M}_{12}(\vec{k},\mathfrak{z})\\ -\underline{M}_{12}(\vec{k},-\mathfrak{z}^*)^* & -(\mathfrak{z}+E_0)\underline{I}-\underline{M}_{11}(\vec{k},-\mathfrak{z}^*)^*\end{vmatrix}^{-1}, \qquad \text{(A14)}$$

where we have used the symmetry relations of Eq. (A10). In Eq. (A14) the (8×8) unit matrix is denoted by $\underline{I}$.

To simplify Eq. (A14) we introduce the 8×8 matrix $\underline{R}$ whose matrix elements are defined by

$$R(M,N)_{\alpha\beta}=\delta_{\alpha\beta}\,\delta_{M,-N}\,. \qquad \text{(A15)}$$

We may now rewrite Eq. (A9) as

$$\underline{R}\,\underline{M}_{11}(\vec{k}\;\mathfrak{z})\underline{R}=\underline{M}_{11}(\vec{k},\mathfrak{z}^*)^*\,, \qquad \text{(A16a)}$$

$$\underline{R}\,\underline{M}_{12}(\vec{k})\underline{R}=\underline{M}_{12}(\vec{k})^*\,, \qquad \text{(A16b)}$$

where we have used the fact that $\underline{M}_{12}$ is independent of $\mathfrak{z}$ in our approximation. Henceforth we will not indicate explicitly the momentum dependence. Using Eq. (A16) we rewrite Eq. (A14) as

$$\underline{G} = \begin{pmatrix} (\mathfrak{z} - E_0)\underline{I} - \underline{M}_{11}(\mathfrak{z}) & -\underline{M}_{12} \\ -\underline{R}\,\underline{M}_{12}\underline{R} & -(\mathfrak{z} + E_0)\underline{I} - \underline{R}\,\underline{M}_{11}(-\mathfrak{z})\underline{R} \end{pmatrix}^{-1} \quad \text{(A17a)}$$

$$= \left\{ \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} \begin{pmatrix} (\mathfrak{z} - E_0)\underline{I} - \underline{M}_{11}(\mathfrak{z}) & -\underline{M}_{12}\underline{R} \\ -\underline{M}_{12}\underline{R} & -(\mathfrak{z} + E_0)\underline{I} - \underline{M}_{11}(-\mathfrak{z}) \end{pmatrix} \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} \right\}^{-1} , \quad \text{(A17b)}$$

where $\underline{O}$ is the (8×8) null matrix. We now separate $\underline{M}_{11}$ into parts even and odd in $\mathfrak{z}$:

$$E_0\underline{I} + \underline{M}_{11}(\mathfrak{z}) = \underline{A}(\mathfrak{z}^2) + \mathfrak{z}\,\underline{C}(\mathfrak{z}^2) , \quad \text{(A18)}$$

where

$$\underline{A}(\mathfrak{z}^2) = E_0\underline{I} + \tfrac{1}{2}[\underline{M}_{11}(\mathfrak{z}) + \underline{M}_{11}(-\mathfrak{z})] \quad \text{(A19a)}$$

and

$$\underline{C}(\mathfrak{z}^2) = (2\mathfrak{z})^{-1}[\underline{M}_{11}(\mathfrak{z}) - \underline{M}_{11}(-\mathfrak{z})] . \quad \text{(A19b)}$$

Then we have that

$$\underline{G} = \left\{ \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} \begin{pmatrix} \mathfrak{z}\underline{I} - \underline{A} - \mathfrak{z}\underline{C} & -\underline{M}_{12}\underline{R} \\ -\underline{M}_{12}\underline{R} & -\mathfrak{z}\underline{I} - \underline{A} + \mathfrak{z}\underline{C} \end{pmatrix} \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} \right\}^{-1} \quad \text{(A20a)}$$

$$= \left\{ \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} \begin{pmatrix} \underline{I} - \underline{C} & \underline{O} \\ \underline{O} & \underline{I} - \underline{C} \end{pmatrix} \begin{pmatrix} \mathfrak{z}\underline{I} - \underline{A}' & -\underline{B}' \\ -\underline{B}' & -\mathfrak{z}\underline{I} - \underline{A}' \end{pmatrix} \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} \right\}^{-1} , \quad \text{(A20b)}$$

where

$$\underline{A}' = (\underline{I} - \underline{C})^{-1}\underline{A} , \quad \text{(A21a)}$$

$$\underline{B}' = (\underline{I} - \underline{C})^{-1}\underline{M}_{12}\underline{R} . \quad \text{(A21b)}$$

The matrix inversion in Eq. (A20) yields

$$\underline{G} = \frac{1}{2} \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} \begin{pmatrix} (\mathfrak{z}\underline{I} + \underline{A}' - \underline{B}')\underline{K}_1^{-1} + (\mathfrak{z}\underline{I} + \underline{A}' + \underline{B}')\underline{K}_2^{-1} & (\mathfrak{z}\underline{I} + \underline{A}' - \underline{B}')\underline{K}_1^{-1} - (\mathfrak{z}\underline{I} + \underline{A}' + \underline{B}')\underline{K}_2^{-1} \\ (-\mathfrak{z}\underline{I} + \underline{A}' - \underline{B}')\underline{K}_1^{-1} \; (\mathfrak{z}\underline{I} - \underline{A}' - \underline{B}')\underline{K}_2^{-1} & (-\mathfrak{z}\underline{I} + \underline{A}' - \underline{B}')\underline{K}_1^{-1} + (-\mathfrak{z}\underline{I} + \underline{A}' + \underline{B}')\underline{K}_2^{-1} \end{pmatrix}$$

$$\times \begin{pmatrix} \underline{I} - \underline{C} & \underline{O} \\ \underline{O} & \underline{I} - \underline{C} \end{pmatrix}^{-1} \begin{pmatrix} \underline{I} & \underline{O} \\ \underline{O} & \underline{R} \end{pmatrix} , \quad \text{(A22)}$$

where

$$\underline{K}_1 = \mathfrak{z}^2\underline{I} - (\underline{A}' + \underline{B}')(\underline{A}' - \underline{B}') , \quad \text{(A23a)}$$

$$\underline{K}_2 = \mathfrak{z}^2\underline{I} - (\underline{A}' - \underline{B}')(\underline{A}' + \underline{B}') . \quad \text{(A23b)}$$

From this discussion it is clear that the quasiparticle energies are given by

$$\mathrm{Re}\,\mathrm{Det}\,\underline{K}_1 = \mathrm{Re}\,\mathrm{Det}\,\underline{K}_2 = 0 . \quad \text{(A24)}$$

Harmonic Approximation

It is instructive to examine the solution of the Dyson equation, using the formalism discussed above, for the situation where the anharmonicity is completely ignored. We will find that we reproduce results found previously by others. In the harmonic approximation we have

$$\underline{C} = 0 , \quad \text{(A25a)}$$

$$\underline{A} = \underline{A}' = E_0\underline{I} + \underline{M}_{11}^0 , \quad \text{(A25b)}$$

$$\underline{B}' = \underline{M}_{12}^0\underline{R} = -\underline{M}_{11}^0 , \quad \text{(A25c)}$$

and we may write $\underline{K}_1 = \underline{K}_2 = \underline{K}$, with $\underline{K}$ defined by

$$\underline{K} = \mathfrak{z}^2\underline{I} - E_0(E_0\underline{I} + 2\underline{M}_{11}^0) . \quad \text{(A25d)}$$

Then it follows from Eq. (A22) that

$$\begin{pmatrix} \underline{G}_{11} & \underline{G}_{12} \\ \underline{G}_{21} & \underline{G}_{22} \end{pmatrix} = \begin{pmatrix} [(\mathfrak{z} + E_0)\underline{I} + \underline{M}_{11}^0]\underline{K}^{-1} & \underline{M}_{11}^0\underline{K}^{-1}\underline{R} \\ \underline{R}\,\underline{M}_{11}^0\underline{K}^{-1} & -\underline{R}[(\mathfrak{z} - E_0)\underline{I} - \underline{M}_{11}^0]\underline{K}^{-1}\underline{R} \end{pmatrix} . \quad \text{(A26)}$$

We denote by $\underline{U}^0(\vec{k})$ the (8×8) unitary matrix which diagonalizes $\underline{M}_{11}^0(\vec{k})$. In the language of transformation theory, $\underline{U}^0(\vec{k})$ is the transformation matrix between the momentum-sublattice and what we call the energy representations. We label the rows of $\underline{U}^0$ by α and M and the columns by an index μ, where $\mu=1,\ldots,8$. Thus the matrix elements of $\underline{U}^0(\vec{k})$ are denoted $U^0(\vec{k})_{\alpha,M;\mu}$. By the definition of $\underline{U}^0(\vec{k})$ we write

$$[\underline{U}^0(\vec{k})^{-1}\underline{M}_{11}^0(\vec{k})\underline{U}^0(\vec{k})]_{\mu\nu}=\delta_{\mu\nu}m_\mu(\vec{k}) \, . \tag{A27}$$

Then the normal-mode energies $E_\mu(\vec{k})$, determined from the eigenvalue equation (A24), are

$$E_\mu(\vec{k})=[E_0(E_0+2m_\mu(\vec{k}))]^{1/2} \, . \tag{A28}$$

An explicit evaluation of $\underline{G}_{\sigma\sigma'}(M;N;\vec{k};\mathfrak{z})$ can be given using $\underline{U}^0(\vec{k})$, and we obtain from Eq. (A27)

$$G_{11}(M,N;\vec{k},\mathfrak{z})_{\alpha\beta}=\sum_\nu U^0(\vec{k})_{\alpha M;\nu}U^0(\vec{k})^*_{\beta N;\nu}\left(\frac{\alpha_\nu^2(\vec{k})}{\mathfrak{z}-E_\nu(\vec{k})}-\frac{\beta_\nu^2(\vec{k})}{\mathfrak{z}+E_\nu(\vec{k})}\right) \quad , \tag{A29a}$$

$$G_{12}(M,N;\vec{k};\mathfrak{z})_{\alpha\beta}=\sum_\nu U^0(\vec{k})_{\alpha M;\nu}U^0(\vec{k})_{\beta N;\nu}\alpha_\nu(k)\beta_\nu(k)\left(\frac{1}{\mathfrak{z}-E_\nu(\vec{k})}-\frac{1}{\mathfrak{z}+E_\nu(\vec{k})}\right) \quad , \tag{A29b}$$

$$G_{21}(M,N;\vec{k};\mathfrak{z})_{\alpha\beta}=\sum_\nu U^0(\vec{k})^*_{\alpha M;\nu}U^0(\vec{k})^*_{\beta N;\nu}\alpha_\nu(k)\beta_\nu(k)\left(\frac{1}{\mathfrak{z}-E_\nu(\vec{k})}-\frac{1}{\mathfrak{z}+E_\nu(\vec{k})}\right) \quad , \tag{A29c}$$

$$G_{22}(M;N;\vec{k};\mathfrak{z})_{\alpha\beta}=\sum_\nu U^0(\vec{k})^*_{\alpha M;\nu}U^0(\vec{k})_{\beta N;\nu}\left(\frac{\beta_\nu^2(\vec{k})}{\mathfrak{z}-E_\nu(\vec{k})}-\frac{\alpha_\nu^2(\vec{k})}{\mathfrak{z}+E_\nu(\vec{k})}\right) \quad , \tag{A29d}$$

where

$$\alpha_\nu^2(\vec{k})=\frac{E_0+m_\nu(k)}{2E_\nu(k)}+\frac{1}{2} \, , \tag{A30a}$$

$$\beta_\nu^2(\vec{k})=\frac{E_0+m_\nu(k)}{2E_\nu(k)}-\frac{1}{2} \, , \tag{A30b}$$

and we have used the result that

$$U^0(\vec{k})_{\alpha M;\nu}=U^0(\vec{k})^*_{\alpha,-M;\nu} \, , \tag{A31}$$

which is a consequence of the fact that

$$\underline{M}_{11}^0(M,N;\vec{k})=\underline{M}_{11}^0(-M,-N;\vec{k})^* \, . \tag{A32}$$

Explicit Anharmonic Calculation for $k=0$

To avoid excessive algebraic complications we now specialize the discussion to zero wave vector $\vec{k}$. From a group-theoretical analysis it is found that the libron modes at $k=0$ transform as E_g+2T_g, where E_g and T_g label the irreducible representations of the group of the wave vector. Since one of the representations is repeated, the symmetry-adapted basis functions will not diagonalize the (8×8) matrix $\underline{M}_{11}$, but will only reduce them to block-diagonal form. The (8×8) matrix $\underline{V}$ which effects this reduction is

$$\underline{V}=\frac{1}{2}\begin{pmatrix} 1 & 0 & 1 & 0 & e^- & 0 & e^+ & 0 \\ 0 & -1 & 0 & -1 & 0 & e^+ & 0 & e^- \\ 0 & -1 & 0 & 1 & 0 & -e^+ & 0 & e^- \\ 0 & 1 & 0 & -1 & 0 & -e^+ & 0 & e^- \\ 0 & 1 & 0 & 1 & 0 & e^+ & 0 & e^- \\ -1 & 0 & -1 & 0 & e^- & 0 & e^+ & 0 \\ -1 & 0 & 1 & 0 & -e^- & 0 & e^+ & 0 \\ 1 & 0 & -1 & 0 & -e^- & 0 & e^+ & 0 \end{pmatrix} \, , \tag{A33}$$

where $e^\pm=e^{\pm 2\pi i/3}$.

The matrices $\underline{M}_{11}$, $\underline{A}$, $\underline{C}$, and $\underline{A}'$ assume the same form and we write for $k=0$

$$\underline{M}_{11}=\begin{pmatrix} w & x & xe^+ & -xe^- & 0 & -y & -y & y \\ x^* & w & y & -y & -y & 0 & -x^*e^+ & x^*e^- \\ x^*e^- & y & w & -y & -y & -x^*e^+ & 0 & x^* \\ -x^*e^+ & -y & -y & w & y & x^*e^- & x^* & 0 \\ 0 & -y & -y & y & w & x^* & x^*e^- & -x^*e^+ \\ -y & 0 & -xe^- & xe^+ & x & w & y & -y \\ -y & -xe^- & 0 & x & xe^+ & y & w & -y \\ y & xe^+ & x & 0 & -xe^- & -y & -y & w \end{pmatrix} \, , \tag{A34}$$

where x denotes $x(\mathfrak{z})$ and x^* denotes $x(\mathfrak{z}^*)^*$. The matrix $\underline{M}_{12}$ is of the form for $k=0$

$$\underline{M}_{12}=\begin{bmatrix} 0 & s & s & -s & -u & -v & -ve^{+} & ve^{-} \\ s & 0 & v^{*}e^{+} & -v^{*}e^{-} & -v^{*} & -u & -s & s \\ s & v^{*}e^{+} & 0 & -v^{*} & -v^{*}e^{-} & -s & -u & s \\ -s & -v^{*}e^{-} & -v^{*} & 0 & v^{*}e^{+} & s & s & -u \\ -u & -v^{*} & -v^{*}e^{-} & v^{*}e^{+} & 0 & s & s & -s \\ -v & -u & -s & s & s & 0 & ve^{-} & -ve^{+} \\ -ve^{+} & -s & -u & s & s & ve^{-} & 0 & -v \\ ve^{-} & s & s & -u & -s & -ve^{+} & -v & 0 \end{bmatrix} \tag{A35}$$

We would like to put the matrices above in block-diagonal form. We shall denote the transformed block-diagonal matrices with carets, so that for any matrix $\underline{M}$ we write

$$\hat{\underline{M}}=\underline{V}^{-1}\underline{M}\,\underline{V}\ . \tag{A36}$$

The block-diagonal forms of $\underline{M}_{11}(k=0)$ and $\underline{M}_{12}(k=0)\underline{R}$ are

$$\hat{\underline{M}}_{11}=\begin{bmatrix} w+3y & & & & & & & \\ & w+3y & & & & & & \\ & & w-y & -2x & & & & \\ & & -2x^{*} & w-y & & & & \\ & & & & w-y & -2x & & \\ & & & & -2x^{*} & w-y & & \\ & & & & & & w-y & -2x \\ & & & & & & -2x^{*} & w-y \end{bmatrix}, \tag{A37}$$

$$\hat{\underline{M}}_{12}\hat{\underline{R}}=-\begin{bmatrix} u+3s & & & & & & & \\ & u+3s & & & & & & \\ & & u-s & -2v & & & & \\ & & -2v^{*} & u-s & & & & \\ & & & & u-s & -2v & & \\ & & & & -2v^{*} & u-s & & \\ & & & & & & u-s & -2v \\ & & & & & & -2v^{*} & u-s \end{bmatrix}. \tag{A38}$$

Since the determinant is invariant under a unitary transformation we may write the eigenvalue equation (A24) as

$$\mathrm{Det}\left|\underline{V}^{-1}\underline{K}_1\underline{V}\right|=\mathrm{Det}\left|\hat{\underline{K}}_1\right|=0\ , \tag{A39}$$

which is written as

$$\mathrm{Det}\left|\mathfrak{z}^2\underline{I}-(\underline{I}-\hat{\underline{C}})^{-1}(\hat{\underline{A}}+\hat{\underline{M}}_{12}\hat{\underline{R}})(\underline{I}-\hat{\underline{C}})^{-1}(\hat{\underline{A}}-\hat{\underline{M}}_{12}\hat{\underline{R}})\right|=0\ . \tag{A40}$$

We shall label the blocks of the transformed matrices by the subscripts e for the (1×1) matrices of E_g symmetry and by t for the (2×2) matrices of T_g symmetry. In this notation we write Eqs. (A37) and (A38) as

$$[\hat{\underline{M}}_{11}]_e=w+3y\ , \tag{A41a}$$

$$[\hat{\underline{M}}_{12}\hat{\underline{R}}]_e=-(u+3s)\ , \tag{A41b}$$

$$[\hat{\underline{M}}_{11}]_t=\begin{bmatrix} w-y & -2y \\ -2x^{*} & w-y \end{bmatrix}, \tag{A41c}$$

$$[\hat{\underline{M}}_{12}\hat{\underline{R}}]_t=-\begin{bmatrix} u-s & -2v \\ -2v^{*} & u-s \end{bmatrix}. \tag{A41d}$$

We separate the harmonic and anharmonic contributions to the matrix elements as follows

$$w(\mathfrak{z}) = w_0 + \delta w(\mathfrak{z}) , \quad \text{(A42a)}$$

$$x(\mathfrak{z}) = x_0 + \delta x(\mathfrak{z}) , \quad \text{(A42b)}$$

$$y(\mathfrak{z}) = y_0 + \delta y(\mathfrak{z}) , \quad \text{(A42c)}$$

$$u = u_0 + \delta u , \quad \text{(A42d)}$$

$$s = s_0 + \delta s , \quad \text{(A42e)}$$

$$v = v_0 + \delta v , \quad \text{(A42f)}$$

where w_0, x_0, ..., etc. are the values of the matrix elements in the harmonic approximation. We have[48, 95]

$$w_0 = u_0 = 0.732\Gamma , \quad \text{(A43a)}$$

$$x_0 = v_0 = (3.070 - 0.552i)\Gamma , \quad \text{(A43b)}$$

$$y_0 = s_0 = -2.311\Gamma , \quad \text{(A43c)}$$

and by comparing Eq. (A8) with Eqs. (A34) and (A35) we find

$$\delta w(\mathfrak{z}) = \frac{9s_2}{2\mathfrak{z}_0} - \frac{s_1}{(2\mathfrak{z}_0 - \mathfrak{z})} - \frac{6s_2}{(3\mathfrak{z}_0 - \mathfrak{z})} , \quad \text{(A44a)}$$

$$\delta x(\mathfrak{z}) = -2s_3/(2\mathfrak{z}_0 - \mathfrak{z}) , \quad \text{(A44b)}$$

$$\delta y(\mathfrak{z}) = -2s_4/(2\mathfrak{z}_0 - \mathfrak{z}) , \quad \text{(A44c)}$$

$$\delta u = 2s_2/\mathfrak{z}_0 , \quad \text{(A44d)}$$

$$\delta v = -s_5/\mathfrak{z}_0 , \quad \text{(A44e)}$$

$$\delta s = -s_6/\mathfrak{z}_0 , \quad \text{(A44f)}$$

where the s_n are lattice sums defined by

$$s_1 = \frac{1}{2} \sum_{M, M', N, j} |\zeta_{ij}^{M'-M, N}|^2 = 84.79\Gamma^2 , \quad \text{(A45a)}$$

$$s_2 = \frac{1}{4} \sum_{M, N, j} |\zeta_{ij}^{M, N}|^2 = 5.95\Gamma^2 , \quad \text{(A45b)}$$

$$s_3 = \frac{1}{2} \sum_{\substack{j \in 2 \\ (i \in 1)}} \sum_{M' N'} \zeta_{ij}^{M'-1, N'*} \zeta_{ij}^{M', N'-1}$$

$$= (4.544 - 8.402i)\Gamma^2 , \quad \text{(A45c)}$$

$$s_4 = -\frac{1}{2} \sum_{\substack{j \in 2 \\ (i \in 1)}} \sum_{M', N'} \zeta_{ij}^{M'-1, N'*} \zeta_{ij}^{M', N'+1}$$

$$= -5.234\Gamma^2 , \quad \text{(A45d)}$$

$$s_5 = -\frac{1}{2} \sum_{\substack{j \in 2 \\ (i \in 1)}} \sum_{M', N'} \zeta_{ij}^{1-M', -1-N'} \zeta_{ij}^{M', N'}$$

$$= (-8.789 + 0.256i) , \quad \text{(A45e)}$$

$$s_6 = \frac{1}{2} \sum_{\substack{j \in 2 \\ (i \in 1)}} \sum_{M', N'} \zeta_{ij}^{1-M', 1-N'} \zeta_{ij}^{M', N'} = 8.098\Gamma^2 . \quad \text{(A45f)}$$

The numerical evaluation of these lattice sums is facilitated by the symmetry relations among the $\zeta_{ij}^{M,N}$ discussed in Ref. 49. In the evaluation we have restricted the sums to nearest neighbors. Since each term in the sum depends on the intermolecular distance R_{ij} as R_{ij}^{-10}, further-than-nearest neighbors can safely be neglected.

We find the explicit forms for the matrices $\underline{A}$ and $\underline{C}$ in terms of these lattice sums s_n:

$$[\hat{\underline{A}}(\mathfrak{z}^2)]_e = E_0 + w_0 + 3y_0 + \frac{9s_2}{2\mathfrak{z}_0} - \frac{2\mathfrak{z}_0(s_1 + 6s_4)}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} - \frac{18\mathfrak{z}_0 s_2}{9\mathfrak{z}_0^2 - \mathfrak{z}^2} , \quad \text{(A46a)}$$

$$[\underline{I} - \hat{\underline{C}}(\mathfrak{z}^2)]_e = 1 + \frac{s_1 + 6s_4}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} + \frac{6s_2}{9\mathfrak{z}_0^2 - \mathfrak{z}^2} , \quad \text{(A46b)}$$

$$[\hat{\underline{A}}(\mathfrak{z}^2)]_t = \begin{pmatrix} E_0 + w_0 - y_0 + \dfrac{9s_2}{2\mathfrak{z}_0} + \mathfrak{z}_0 \dfrac{4s_4 - 2s_1}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} - \dfrac{18\mathfrak{z}_0 s_2}{9\mathfrak{z}_0^2 - \mathfrak{z}^2} & -2x_0 + \dfrac{8\mathfrak{z}_0 s_3}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} \\ -2x_0^* + \dfrac{8\mathfrak{z}_0 s_3^*}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} & E_0 + w_0 - y_0 + \dfrac{9s_2}{2\mathfrak{z}_0} + \mathfrak{z}_0 \dfrac{4s_4 - 2s_1}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} - \dfrac{18\mathfrak{z}_0 s_2}{9\mathfrak{z}_0^2 - \mathfrak{z}^2} \end{pmatrix} , \quad \text{(A46c)}$$

$$[\hat{\underline{C}}(\mathfrak{z}^2)]_t = \begin{pmatrix} \dfrac{2s_4 - s_1}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} - \dfrac{6s_2}{9\mathfrak{z}_0^2 - \mathfrak{z}^2} & \dfrac{4s_3}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} \\ \dfrac{4s_3^*}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} & \dfrac{2s_4 - s_1}{4\mathfrak{z}_0^2 - \mathfrak{z}^2} - \dfrac{6s_2}{9\mathfrak{z}_0^2 - \mathfrak{z}^2} \end{pmatrix} \quad \text{(A46d)}$$

Using these results and also Eq. (A41) we can evaluate the eigenvalue equation (A40). For the E_g mode we have

$$f(z)=\mathfrak{z}^2-\left(1+\frac{s_1+6s_4}{4\mathfrak{z}_0^2-\mathfrak{z}^2}+\frac{6s_2}{9\mathfrak{z}_0^2-\mathfrak{z}^2}\right)^{-2} \times\left[\left(E_0+w_0+3y_0+\frac{9s_2}{2\mathfrak{z}_0}-\frac{2\mathfrak{z}_0(s_1+6s_4)}{4\mathfrak{z}_0^2-\mathfrak{z}^2}-\frac{18\mathfrak{z}_0 s_2}{9\mathfrak{z}_0^2-\mathfrak{z}^2}\right)^2-\left(w_0+3y_0+\frac{2s_2-3s_6}{\mathfrak{z}_0}\right)^2\right]=0\ . \quad \text{(A47)}$$

The secular equation for the T_g modes is quite complicated and was solved numerically.

APPENDIX B: CALCULATION OF RAMAN INTENSITIES

General Formulation

In this appendix we shall obtain formulas and numerical results for the Raman intensities of the single-libron lines. The calculation consists of two steps; first we express the Raman intensities in terms of the spectral weight functions associated with the single-particle Green's functions, and then by use of the symmetry coordinates discussed in Appendix A we are able to numerically evaluate the formulas we derive for the Raman intensities.

It can be shown that the transition probability per unit time, $W(\vec{k},\omega)$, that a system makes a transition from an initial state to a final state with the transfer of energy $\hbar\omega$ and momentum $\vec{k}$ due to an external perturbation may be conveniently expressed in the form of a temporal Fourier transform of a correlation function.[81,82] For the particular case of light scattering, in which the interaction of the radiation field with the crystal is treated in the polarizability approximation,[81] we may write the perturbation as

$$\mathcal{H}_{\text{int}}=\frac{1}{2}\sum_i\sum_{MN}C(112;M,N-M)\alpha_N^{(2)}(\vec{R}_i)^*E_ME_{N-M}\ , \quad \text{(B1)}$$

where $\alpha_N^{(2)}(\vec{R}_i)$ is the Nth spherical component of the polarizability tensor for the ith molecule and E_M is the Mth spherical component of the external field at the position of the ith molecule. In this case the transition probability $W(\vec{k},\omega)$ for unpolarized incident radiation and a powder sample takes the form[81]

$$W(\vec{k},\omega)=\hbar c^2k_Ik_SV^{-2}\sum_{i,j}\sum_M e^{-i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} \times\int_{-\infty}^{+\infty}dt\,e^{i\omega t}\langle\alpha_M^{(2)}(\vec{R}_i,t)\alpha_M^{(2)}(\vec{R}_j,0)^*\rangle\ , \quad \text{(B2)}$$

where $\alpha_M^{(2)}(\vec{R}_i,t)$ is a time-dependent operator in the Heisenberg picture. The momenta of the incident and scattered photon are denoted by $\vec{k}_I$ and $\vec{k}_S$, respectively, and $\vec{k}=\vec{k}_I-\vec{k}_S$. In Eq. (B2) we have the desired expression relating the transition probability to the Fourier transform of the polarizability-polarizability correlation function.

We have shown previously[49] that

$$\alpha_M^{(2)}(\vec{R}_j)=3\kappa\,\overline{\alpha}\left(\frac{8\pi}{15}\right)^{1/2}\sum_{M'}D_{MM'}^{(2)}(\hat{\chi}_j)^*Y_2^{M'}(\hat{\omega}_j)\ , \quad \text{(B3)}$$

where $\overline{\alpha}$ is the average polarizability and κ is the anisotropy of the polarizability. With the use of Eq. (B3) the transition probability becomes

$$W(\vec{k},\omega)=\hbar c^2k_Ik_SV^{-2}\frac{24\pi}{5}(\kappa\overline{\alpha})^2\sum_{i,j}\sum_{M,N}D_{NM}^{(2)}(\hat{\chi}_{ji})^* \times e^{-i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)}\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle Y_2^M(\hat{\omega}_i,t)Y_2^N(\hat{\omega}_j,0)^*\rangle\ , \quad \text{(B4)}$$

where $\hat{\chi}_{ji}$ are the Euler angles specifying the local axes of molecule i relative to the local axes of molecule j.

Let us define the correlation function $Q(i,M;j,N;t)$ by

$$Q(i,M;j,N;t)=(20\pi/3)\langle Y_2^{-M}(\hat{\omega}_i,t)Y_2^N(\hat{\omega}_j)\rangle \quad \text{(B5)}$$

and its frequency and wave-vector-dependent Fourier transform $Q(M,N;\vec{k},\omega)_{\alpha\beta}$ by

$$Q(M,N;\vec{k},\omega)_{\alpha\beta}=\sum_{\substack{j\in\beta\\(i\in\beta)}}e^{-i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)}\int_{-\infty}^{\infty}dt\,e^{i\omega t} \times Q(i,M;j,N;t)\ . \quad \text{(B6)}$$

Then the transition probability is

$$W(\vec{k},\omega)=\tfrac{18}{25}\hbar c^2V^{-2}k_Ik_S(\kappa\overline{\alpha})^2N_0\sum_{\substack{\alpha,\beta\\M,N}}D_{NM}^{(2)}(\hat{\chi}_{\beta\alpha})^*(-1)^NQ(-M,-N;\vec{k},\omega)_{\alpha\beta}\ . \quad \text{(B7)}$$

The correlation functions $Q(M,N;\vec{k},\omega)_{\alpha\beta}$ can be related to the following imaginary-time Green's functions:

$$P(i,M;j,N;t)=\tfrac{20}{3}\pi i\langle T[Y_2^{-M}(\hat{\omega}_i,t)Y_2^N(\hat{\omega}_j,0)]\rangle\ , \quad \text{(B8)}$$

where T here is the time-ordering operator.[74] We also define the frequency-dependent Green's functions through the Fourier coefficients

$$P(i, M, j, N; \mathfrak{z}_r) = \int_0^{-i\beta} e^{i\mathfrak{z}_r t} P(i, M; j, N; t)\, dt\,, \qquad \text{(B9)}$$

where $\mathfrak{z}_r = \pi i r/\beta$, with r an even integer.

By the general theory of Green's functions[74] we have

$$\underline{Q}(M, N; \vec{k}, \omega) = \frac{1}{2\pi i}\left[1 - e^{-\beta\omega}\right]^{-1} \lim_{\delta\to 0^+}\left[\underline{P}(M, N; \vec{k}, \omega + i\delta) - \underline{P}(M, N; \vec{k}, \omega - i\delta)\right] \qquad \text{(B10)}$$

and in particular, at zero temperature, we have

$$\underline{Q}(M, N; \vec{k}, \omega) = -\theta(\omega)\, \mathrm{Res}[\underline{P}(M, N; \vec{k}, \omega)]\,, \qquad \text{(B11)}$$

where $\theta(\omega) = \frac{1}{2}(\omega + |\omega|)/\omega$ and Res indicates the residue in the case where the Green's function has only poles, but more generally is the discontinuity across the real axis as indicated in Eq. (B10).

With the use of Eqs. (2.6) and (2.12) we write the correlation function of Eq. (B5) in terms of the operators c_{iM} and $c^\dagger_{iM}$. There are contributions to the transition probability which may be interpreted as the scattering of photons with the simultaneous excitation of two librons. [These are the M, $N = 0$, ± 2 terms in Eq. (B7).] Since we are interested in the transition probability at essentially zero temperature, these two-libron processes depend on the zero-point disorder in the system which is known to be quite small. In fact, Nakamura and Miyagi[50] have calculated the Raman intensity from these two-libron processes and have shown it to be very small. We shall therefore neglect these processes here. Thus we restrict ourselves to the terms M, $N = \pm 1$ in Eq. (B5). Then the Raman intensity is determined by the Green's functions,

$$P(M, N; \vec{k}, t)_{\alpha\beta} = i\langle [c_{\alpha,-M}(-\vec{k}, t) - c_{\alpha,M}(\vec{k}, t)] \times [c^\dagger_{\beta,N}(\vec{k}) - c_{\beta,-N}(-\vec{k})]\rangle \qquad \text{(B12)}$$

with t in the interval $(0, -i\beta)$.

In order to evaluate these Green's functions, we may relate them to those of Appendix A. If we expand the operator product in Eq. (B12), we see upon comparison with Eq. (A11) that

$$P(M, N; \vec{k}, t)_{\alpha\beta} = +G_{11}(M, N; \vec{k}, t)_{\alpha\beta} - G_{12}(M, -N; \vec{k}, t)_{\alpha\beta} - G_{21}(-M, N; \vec{k}; t)_{\alpha\beta} + G_{22}(-M, -N; \vec{k}, t)_{\alpha\beta}\,. \qquad \text{(B13)}$$

If we use the matrix $\underline{R}$ introduced in Eq. (A15), we may write

$$\underline{P}(\vec{k}, t) = +\underline{G}_{11}(\vec{k}, t) - \underline{G}_{12}(\vec{k}, t)\underline{R} - \underline{R}\,\underline{G}_{21}(\vec{k}, t) + \underline{R}\,\underline{G}_{22}(\vec{k}, t)\underline{R}\,. \qquad \text{(B14)}$$

By using Eq. (A23) and taking the temporal Fourier transform of Eq. (B14) we find

$$\underline{P}(\vec{k}, \omega) = [\underline{A}'(\vec{k}, \omega) + \underline{B}'(\vec{k}, \omega)]\underline{K}_2^{-1}(\vec{k}, \omega)[\underline{I} - \underline{C}(\vec{k}, \omega)]^{-1}\,. \qquad \text{(B15)}$$

Furthermore the summation in Eq. (B7) is in the form of a matrix product, if we define the (8×8) matrix $D(M, N)_{\alpha\beta}$ by

$$D(M, N)_{\alpha\beta} = (-1)^{M+1} D^{(2)}_{-M,-N}(\hat{\chi}_{\alpha\beta})^*\,. \qquad \text{(B16)}$$

Explicitly we have

$$\underline{D} = \begin{pmatrix} 1 & \frac{2}{9}e^+ & \frac{2}{9}e^- & -\frac{2}{9} & 0 & -\frac{5}{9} & -\frac{5}{9} & \frac{5}{9} \\ \frac{2}{9}e^- & 1 & \frac{5}{9} & -\frac{5}{9} & -\frac{5}{9} & 0 & -\frac{2}{9} & \frac{2}{9}e^+ \\ \frac{2}{9}e^+ & \frac{5}{9} & 1 & -\frac{5}{9} & -\frac{5}{9} & -\frac{2}{9} & 0 & \frac{2}{9}e^- \\ -\frac{2}{9} & -\frac{5}{9} & -\frac{5}{9} & 1 & \frac{5}{9} & \frac{2}{9}e^+ & \frac{2}{9}e^- & 0 \\ 0 & -\frac{5}{9} & -\frac{5}{9} & \frac{5}{9} & 1 & \frac{2}{9}e^- & \frac{2}{9}e^+ & -\frac{2}{9} \\ -\frac{5}{9} & 0 & -\frac{2}{9} & \frac{2}{9}e^- & \frac{2}{9}e^+ & 1 & \frac{5}{9} & -\frac{5}{9} \\ -\frac{5}{9} & -\frac{2}{9} & 0 & \frac{2}{9}e^+ & \frac{2}{9}e^- & \frac{5}{9} & 1 & -\frac{5}{9} \\ \frac{5}{9} & \frac{2}{9}e^- & \frac{2}{9}e^+ & 0 & -\frac{2}{9} & -\frac{5}{9} & -\frac{5}{9} & 1 \end{pmatrix}\,. \qquad \text{(B17)}$$

We can thus write the intensity $W(\vec{k}, \omega)$ as

$$W(\vec{k}, \omega) = \tfrac{18}{25}\hbar c^2 V^{-2} k_I\, k_S (\kappa\,\overline{\alpha})^2 N_0 \times \sum_{\substack{M,N\\ \alpha,\beta}} D(N, M)_{\beta\alpha} Q(M, N; \vec{k}, \omega)_{\alpha\beta} \qquad \text{(B18a)}$$

$$= \tfrac{18}{25}\hbar c^2 V^{-2} k_I k_S (\kappa\bar{\alpha})^2 N_0 \,\mathrm{Tr}[\underline{D}\,\underline{Q}(\vec{k},\omega)]\,, \quad \text{(B18b)}$$

and at zero temperature we have that

$$W(\vec{k},\omega) = \tfrac{18}{25}\hbar c^2 V^{-2} N_0 k_I k_S (\kappa\bar{\alpha})^2 \,\mathrm{Res}\,\mathrm{Tr}[\underline{D}\,\underline{P}(\vec{k},\omega)] \quad \text{(B18c)}$$

$$= \tfrac{18}{25}\hbar c^2 V^{-2} N_0 k_I k_S (\kappa\bar{\alpha})^2 \,\mathrm{Res}\,\mathrm{Tr}\{\underline{D}[\underline{A}'(\vec{k},\omega) + \underline{B}'(\vec{k},\omega)]\underline{K}_2^{-1}(\vec{k},\omega)[\underline{I} - \underline{C}(\vec{k},\omega)]^{-1}\}\,. \quad \text{(B18d)}$$

Raman Intensity at $k=0$

We now specialize to consider $W(\vec{k},\omega)$ for $k=0$. We may use the results for $\underline{A}'(\vec{k},\omega)$, $\underline{B}'(\vec{k},\omega)$, and $\underline{C}(\vec{k},\omega)$ for $k=0$ in Appendix A to rewrite Eq. (B18d) as

$$W(0,\omega) = C_0 \,\mathrm{Res}\,\mathrm{Tr}\{\hat{\underline{D}}[\hat{\underline{A}}'(\omega) + \hat{\underline{B}}'(\omega)]\hat{\underline{K}}_2^{-1}[\underline{I} - \hat{\underline{C}}(\omega)]\}\,, \quad \text{(B19)}$$

where we have used the symmetry-adapted coordinates to put the (8×8) matrices in block-diagonal form.

For the E_g modes

$$[\hat{D}]_e = \tfrac{8}{3} \quad \text{(B20)}$$

and the results for $[\hat{A}']_e$ and $[\hat{B}']_e$ are given in Appendix A. Hence

$$W_e(0,\omega) = 2C_0 \,\mathrm{Res}[\hat{D}_e][\hat{A}' + \hat{B}']_e[\hat{K}_2^{-1}]_e[I - \hat{C}]_e^{-1}\big|_{\omega=\omega_e}\,, \quad \text{(B21)}$$

where ω_e denotes the frequency of the E_g mode. This expression was evaluated numerically and the results are given in Table IV.

For the three-fold degenerate T_g levels which we label $T_g^{(\pm)}$ we have

$$[\hat{\underline{D}}]_t = \frac{4}{9}\begin{bmatrix} 1 & -e^+ \\ -e^- & 1 \end{bmatrix}\,. \quad \text{(B22)}$$

The intensity $W_t^{\pm}(0,\omega)$ for the $T_g^{(\pm)}$ modes is given by

$$W_t^{\pm}(0,\omega) = 3C_0 \,\mathrm{Res}\,\mathrm{Tr}\{[\hat{\underline{D}}]_t[\hat{\underline{A}}' + \hat{\underline{B}}']_t[\hat{\underline{K}}_2^{-1}]_t \times [\underline{I} - \hat{\underline{C}}]_t^{-1}\}\big|_{\omega=\omega_\pm}\,. \quad \text{(B23)}$$

The evaluation of $W_t^{\pm}(0,\omega)$ is rather involved since it requires taking the residue of a complicated matrix expression. We show below that the taking of the residue can be separated from the matrix operations.

Consider the (2×2) matrices $\underline{L}$, $\underline{M}$, and $\underline{N}$:

$$\underline{L} = [\underline{I} - \hat{\underline{C}}]_t^{-1}\,, \quad \text{(B24a)}$$

$$\underline{M} = [\hat{\underline{A}} + \hat{\underline{M}}_{12}\hat{\underline{R}}]_t\,, \quad \text{(B24b)}$$

$$\underline{N} = [\hat{\underline{A}} - \hat{\underline{M}}_{12}\hat{\underline{R}}]_t\,, \quad \text{(B24c)}$$

and we write

$$W_t^{\pm}(0,\omega) = 3C_0 \,\mathrm{Res}\,\mathrm{Tr}\underline{S}\,, \quad \text{(B25)}$$

where

$$\underline{S} = [\hat{\underline{D}}]_t\,\underline{L}\,\underline{M}(\omega^2\underline{I} - \underline{L}\,\underline{N}\,\underline{L}\,\underline{M})^{-1}\underline{L}\,. \quad \text{(B26)}$$

We write $\underline{S}$ in the form

$$\underline{S} = [\hat{\underline{D}}]_t\,\underline{L}\,\underline{M}^{1/2}(\omega^2\underline{I} - \underline{M}^{1/2}\underline{L}\,\underline{N}\,\underline{L}\,\underline{M}^{1/2})^{-1}\underline{M}^{1/2}\underline{L}\,. \quad \text{(B27)}$$

Providing $\underline{M}^{1/2}$ can be defined, this relation can be verified by showing that the right-hand sides of Eqs. (B26) and (B27) agree to all orders in ω^{-2}. In order to define $\underline{M}^{1/2}$, $\underline{M}$ must be a positive matrix,[96] i.e., it must have positive eigenvalues. This condition is certainly fulfilled for (ω/E_0) of order unity, since then $\underline{A} + \underline{M}_{12}\underline{R} \approx E_0\underline{I}$, as can be seen from Eqs. (A46) and (A41).

Next, we note that all matrices appearing in Eq. (B27) are of the form

$$\underline{R} = \pm\begin{bmatrix} |a| & b \\ b^* & |a| \end{bmatrix}\,, \quad \text{(B28)}$$

so that

$$\underline{R}^{-1} = (\mathrm{Det}\,\underline{R})^{-1}\sigma_x\,\underline{R}\,\sigma_x\,, \quad \text{(B29)}$$

where σ_x is the Pauli matrix. Thus we may write

$$\underline{S} = \Delta^{-1}\hat{\underline{D}}_t\,\underline{L}\,\underline{M}^{1/2}\sigma_x(\omega^2\underline{I} - \underline{M}^{1/2}\underline{L}\,\underline{N}\,\underline{L}\,\underline{M}^{1/2})\sigma_x\underline{M}^{1/2}\underline{L}\,, \quad \text{(B30)}$$

where

$$\Delta = \mathrm{Det}(\omega^2\underline{I} - \underline{M}\,\underline{L}\,\underline{N}\,\underline{L})\,. \quad \text{(B31)}$$

Also, for matrices $\underline{R}$ of the form of Eq. (B28) one has

$$\underline{R}\,\sigma_x\,\underline{R} = (\mathrm{Det}\underline{R})\sigma_x\,. \quad \text{(B32)}$$

Repeated use of this relation yields

$$\underline{S} = \Delta^{-1}[\omega^2\hat{\underline{D}}_t\,\underline{L}\,\underline{M}\,\underline{L} - (\mathrm{Det}\underline{M})(\mathrm{Det}\underline{L})^2\hat{\underline{D}}_t\,\sigma_x\,\underline{N}\,\sigma_x]\,, \quad \text{(B33)}$$

so that finally we obtain

$$W_t^{\pm}(0,\omega) = 3C_0 \,\mathrm{Res}(\Delta^{-1})\big|_{\omega=\omega_\pm} \times \mathrm{Tr}[\omega^2\hat{\underline{D}}_t\,\underline{L}\,\underline{M}\,\underline{L} - (\mathrm{Det}\underline{M})(\mathrm{Det}\underline{L})^2\hat{\underline{D}}_t\,\sigma_x\underline{N}\,\sigma_x]\,. \quad \text{(B34)}$$

The advantage of this formulation is that the taking of the residue is separated from the matrix operations. In addition, the residue of Δ^{-1}, denoted $\mathrm{Res}(\Delta^{-1})$, at $\omega = \omega_\pm$ is $[(\partial\Delta/\partial\omega)_{\omega=\omega_\pm}]^{-1}$, a quantity which is a natural byproduct of a numerical search for the eigenvalues $\omega_\pm$. The final result is therefore

$$W_t^{\pm}(0,\omega)=3C_0\left[\left(\frac{\partial\Delta}{\partial\omega}\right)_{\omega=\omega_\pm}\right]^{-1}\mathrm{Tr}\{\underline{\hat{D}}_t(\underline{I}-\underline{\hat{C}}_t)^{-1}[\underline{\hat{A}}_t+(\underline{\hat{M}}_{12}\underline{\hat{R}})_t](\underline{I}-\underline{\hat{C}}_t)^{-1}\omega^2-\mathrm{Det}[\underline{\hat{A}}_t+(\underline{\hat{M}}_{12}\underline{\hat{R}})_t]\mathrm{Det}[\underline{I}-\underline{\hat{C}}_t]^{-2}\underline{\hat{D}}_t\underline{\sigma}_z$$
$$\times[\underline{\hat{A}}_t-(\underline{\hat{M}}_{12}\underline{\hat{R}})_t]\underline{\sigma}_z\}|_{\omega=\omega_\pm}\ . \qquad \text{(B35)}$$

APPENDIX C: SYMMETRY PROPERTIES OF GREEN'S FUNCTIONS

In this appendix we derive some symmetry relations for the Green's functions. From the definition of Eqs. (3.2) and (3.3) we obtain after analytic continuation into the complex $\mathfrak{z}$ plane the explicit representations

$$G_{11}(i,M;j,N;\mathfrak{z})=\sum_{m,n}P_n\left(\frac{\langle n|c_{iM}|m\rangle\langle m|c_{jN}^\dagger|n\rangle}{\mathfrak{z}+E_n-E_m}-\frac{\langle n|c_{jN}^\dagger|m\rangle\langle m|c_{iM}|n\rangle}{\mathfrak{z}+E_m-E_n}\right)\ , \qquad \text{(C1a)}$$

$$G_{12}(i,M;j,N;\mathfrak{z})=\sum_{m,n}P_n\left(\frac{\langle n|c_{iM}|m\rangle\langle m|c_{jN}|n\rangle}{\mathfrak{z}+E_n-E_m}-\frac{\langle n|c_{jN}|m\rangle\langle m|c_{iM}|n\rangle}{\mathfrak{z}+E_m-E_n}\right)\ , \qquad \text{(C1b)}$$

$$G_{21}(i,M;j,N;\mathfrak{z})=\sum_{m,n}P_n\left(\frac{\langle n|c_{iM}^\dagger|m\rangle\langle m|c_{jN}^\dagger|n\rangle}{\mathfrak{z}+E_n-E_m}-\frac{\langle n|c_{jN}^\dagger|m\rangle\langle m|c_{iN}^\dagger|n\rangle}{\mathfrak{z}+E_m-E_n}\right)\ , \qquad \text{(C1c)}$$

$$G_{22}(i,M;j,N;\mathfrak{z})=\sum_{m,n}P_n\left(\frac{\langle n|c_{iM}^\dagger|m\rangle\langle m|c_{jN}|n\rangle}{\mathfrak{z}+E_n-E_m}-\frac{\langle n|c_{jN}|m\rangle\langle m|c_{iM}^\dagger|n\rangle}{\mathfrak{z}+E_m-E_n}\right)\ , \qquad \text{(C1d)}$$

where $|n\rangle$ and $|m\rangle$ are eigenstates of the Hamiltonian and P_n is the canonical probability of the state $|n\rangle$:

$$P_n=e^{-\beta E_n}\Big/\textstyle\sum_n e^{-\beta E_n}\ , \qquad \text{(C2)}$$

where $\beta\equiv(kT)^{-1}$. From Eqs. (C1a) and (C1d) it is clear that $\underline{G}_{11}$ and $\underline{G}_{22}$ are Hermitian:

$$G_{11}(i,M;j,N;\mathfrak{z})^*=G_{11}(j,N;i,M;\mathfrak{z}^*)\ , \qquad \text{(C3a)}$$

$$G_{22}(i,M;j,N;\mathfrak{z})^*=G_{22}(j,N;i,M;\mathfrak{z}^*)\ . \qquad \text{(C3b)}$$

In addition we have

$$G_{11}(i,M;j,N;-\mathfrak{z})=G_{22}(j,N;i,M;\mathfrak{z})\ . \qquad \text{(C4)}$$

Combining Eqs. (C3b) and (C4) we obtain

$$G_{22}(i,M;j,N;\mathfrak{z})=G_{11}(i,M;j,N;-\mathfrak{z}^*)^*\ . \qquad \text{(C5)}$$

From Eqs. (C1b) and (C1c) we find that $\underline{G}_{12}$ and $\underline{G}_{21}$ are symmetric:

$$G_{12}(i,M;j,N;\mathfrak{z})=G_{12}(j,N;i,M;-\mathfrak{z})\ , \qquad \text{(C6a)}$$

$$G_{21}(i,M;j,N;\mathfrak{z})=G_{21}(j,N;i,M;-\mathfrak{z})\ . \qquad \text{(C6b)}$$

We also find that

$$G_{12}(i,M;j,N;\mathfrak{z})^*=G_{21}(j,N;i,M;\mathfrak{z}^*)\ . \qquad \text{(C7)}$$

Combining Eqs. (C6a) and (C7) we have that

$$G_{12}(i,M;j,N;\mathfrak{z})=G_{21}(i,M;j,N;-\mathfrak{z}^*)^*\ . \qquad \text{(C8)}$$

Let us now discuss the symmetry between the $J_z=1$ and $J_z=-1$ excitations. From Eq. (2.10) we see that

$$\zeta_{ij}^{M,N*}=(-1)^{M+N}\zeta_{ij}^{-M,-N}\ . \qquad \text{(C9)}$$

Using Eq. (C9) we see that the Hamiltonian of Eq. (2.14) has the following symmetry:

$$\mathcal{H}(c_{iM},c_{iM}^\dagger)=\mathcal{H}(c_{i,-M},c_{i,-M}^\dagger)^*\ . \qquad \text{(C10)}$$

Note that the eigenfunctions of $\mathcal{H}^*$ are just the complex conjugates of those of $\mathcal{H}$. This enables us to write

$$G_{11}(i,M;j,N;\mathfrak{z})^*=G_{11}(i,-M;j,-N;\mathfrak{z}^*)\ . \qquad \text{(C11)}$$

Similar reasoning heads to the relation

$$G_{12}(i,M;j,N;\mathfrak{z})^*=G_{12}(i,-M;j,-N;\mathfrak{z}^*)\ . \qquad \text{(C12)}$$

In matrix notation we may write

$$\underline{R}\,\underline{G}_{\sigma\sigma'}(\mathfrak{z})^*\underline{R}=\underline{G}_{\sigma\sigma'}(\mathfrak{z}^*)\ . \qquad \text{(C13)}$$

Finally, we note that each site possesses inversion symmetry. Moreover, inversion leaves the sublattice labeling invariant. We therefore conclude that all spatial Fourier transforms will be even functions of $\vec{k}$. Hence all the relations of this appendix hold when the site indices $\vec{R}_i$ and $\vec{R}_j$ are replaced by the Fourier transform variable $\vec{k}$.

The analagous relations hold for the self-energy:

$$M_{11}(M,N;\vec{k},\mathfrak{z})^*_{\alpha\beta}=M_{11}(N,M;\vec{k},\mathfrak{z}^*)_{\beta\alpha}\ , \qquad \text{(C14a)}$$

$$M_{22}(M,N;\vec{k},\mathfrak{z})^*_{\alpha\beta}=M_{11}(N,M;\vec{k},\mathfrak{z}^*)_{\beta\alpha}\ , \qquad \text{(C14b)}$$

$$M_{11}(M,N;\vec{k},\mathfrak{z})_{\alpha\beta}=M_{22}(N,M;\vec{k},-\mathfrak{z})_{\beta\alpha}\ , \qquad \text{(C15a)}$$

$$M_{22}(M,N;\vec{k},\mathfrak{z})_{\alpha\beta}=M_{11}(M,N;\vec{k},-\mathfrak{z}^*)^*_{\alpha\beta}\ , \qquad \text{(C15b)}$$

$$M_{12}(M, N; \vec{k}, \mathfrak{z})_{\alpha\beta} = M_{12}(N, M; \vec{k}, -\mathfrak{z})_{\beta\alpha}\,, \tag{C16a}$$

$$M_{21}(M, N; \vec{k}, \mathfrak{z})_{\alpha\beta} = M_{21}(N, M; \vec{k}, -\mathfrak{z})_{\beta\alpha}\,, \tag{C16b}$$

$$M_{12}(M, N; \vec{k}, \mathfrak{z})^*_{\alpha\beta} = M_{21}(N, M; \vec{k}, \mathfrak{z}^*)_{\beta\alpha}\,, \tag{C17a}$$

$$M_{21}(M, N; \vec{k}, \mathfrak{z})_{\alpha\beta} = M_{12}(M, N; \vec{k}, -\mathfrak{z}^*)^*_{\alpha\beta}\,, \tag{C17b}$$

$$\underline{R}\,\underline{M}_{\sigma\sigma'}(\vec{k}, \mathfrak{z})\underline{R} = \underline{M}_{\sigma\sigma'}(\vec{k}, \mathfrak{z}^*)^*\,. \tag{C18}$$

APPENDIX D: EVALUATION OF SUM RULES FOR RAMAN INTENSITY

In this appendix we shall obtain expressions for the coefficients of the large-$\mathfrak{z}$ asymptotic expansion for the response function which determines the Raman intensity.

From Appendix B it is clear that we may write

$$W(\vec{k}, \omega) = (1 - e^{-\beta\omega})^{-1} \frac{1}{2\pi i} (2C_0)[H(\omega + i0^+) - H(\omega - i0^+)]\,, \tag{D1}$$

where

$$H(\mathfrak{z}) = \sum_{\alpha,\beta} \sum_{M,N}{}' D(N, M)_{\beta\alpha} P(M, N; \vec{k}, \mathfrak{z})_{\alpha\beta}\,; \tag{D2}$$

from Appendix B we see that

$$P(M, N; \vec{k}, \mathfrak{z}_r)_{\alpha\beta} = \frac{-20\pi i}{3} \sum_{\substack{j\in\alpha\\(i\in\beta)}} e^{-i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)} \times \int_0^{-i\beta} e^{i\mathfrak{z}_r t} \langle T[Y_2^{-M}(\omega_i, t) Y_2^N(\omega_j, 0)]\rangle\, dt\,, \tag{D3}$$

from which it may be shown that

$$P(M, N; \vec{k}, \mathfrak{z})_{\alpha\beta} = P(-N, -M, \vec{k}, -\mathfrak{z})_{\beta\alpha}\,. \tag{D4}$$

The matrix $\underline{D}$ also satisfies the relation

$$D(-M, -N)_{\alpha\beta} = D(N, M)_{\beta\alpha}\,. \tag{D5}$$

With the use of Eqs. (D4) and (D5) it follows that $H(\mathfrak{z})$ is an even function of $\mathfrak{z}$ and consequently has the asymptotic expansion

$$H(\mathfrak{z}) = M_1(\mathfrak{z})^{-2} + M_3(\mathfrak{z})^{-4} + \cdots\,. \tag{D6}$$

Determining the coefficients in this expansion from Eq. (4.10) we obtain Eqs. (4.12) and (4.13) in the text.

Within the approximations of this work we have

$$H(\mathfrak{z}) = \tfrac{1}{2}\,\mathrm{Tr}\{\underline{D}(\underline{A}' + \underline{B}')[\mathfrak{z}^2\underline{I} - (\underline{A}' - \underline{B}') \times (\underline{A}' + \underline{B}')]^{-1}(\underline{I} - \underline{C})^{-1}\} \tag{D7}$$

as in Eq. (B18). We shall obtain explicit expressions for M_1 and M_3 by constructing the large-$\mathfrak{z}$ expansion of $H(\mathfrak{z})$ using this representation. For this purpose we need keep only terms of order $\mathfrak{z}^{-2}$ and $\mathfrak{z}^{-4}$.

The simplest case is when Rayleigh-Schrödinger perturbation theory is used. Then, as in the harmonic case, the dynamical matrix is frequency independent, and the large-$\mathfrak{z}$ expansion is obtained by expanding the matrix inverse in Eq. (D7) in a geometric series. Thus, for the frequency-independent cases we have

$$M_1 = \tfrac{1}{2}\,\mathrm{Tr}[\underline{D}(\underline{A}' + \underline{B}')(\underline{I} - \underline{C})^{-1}]\,, \tag{D8}$$

$$M_3 = \tfrac{1}{2}\,\mathrm{Tr}[\underline{D}(\underline{A}' + \underline{B}')(\underline{A}' - \underline{B}')(\underline{A}' + \underline{B}')(\underline{I} - \underline{C})^{-1}]\,. \tag{D9}$$

More generally, the matrices in Eq. (D7) are frequency dependent. In fact, since $\underline{C}$ is of order $\mathfrak{z}^{-2}$, we may use

$$(\underline{I} - \underline{C})^{-1} = \underline{I} + \underline{C}_2\mathfrak{z}^{-2}\,, \tag{D10}$$

where $\underline{C}_2$ is the coefficient of $\mathfrak{z}^{-2}$ in the Laurent expansion of $\underline{C}(\mathfrak{z})$. Later $\underline{A}_2$ is defined similarly. In addition, we recall Eq. (A21):

$$\underline{A}' + \underline{B}' = (\underline{I} - \underline{C})^{-1}(\underline{A} + \underline{M}_{12}\underline{R})\,. \tag{D11}$$

Using these relations we obtain the results

$$M_1 = \tfrac{1}{2}\,\mathrm{Tr}\{\underline{D}[\underline{A}(\infty) + \underline{M}_{12}(\infty)\underline{R}]\}\,, \tag{D12a}$$

$$M_3 = \tfrac{1}{2}\,\mathrm{Tr}(\underline{D}\{\underline{C}_2[\underline{A}(\infty) + \underline{M}_{12}(\infty)\underline{R}] + [\underline{A}(\infty) + \underline{M}_{12}(\infty)\underline{R}]\underline{C}_2 + \underline{A}_2 + [\underline{A}(\infty) + \underline{M}_{12}(\infty)\underline{R}][\underline{A}(\infty) - \underline{M}_{12}(\infty)\underline{R}] \times [\underline{A}(\infty) + \underline{M}_{12}(\infty)\underline{R}]\})\,, \tag{D12b}$$

where we have dropped $\underline{B}_2$, since it vanishes within our approximations.

Since the response function is actually the sum of independent response functions for each type of symmetry, we can obtain separate sum rules for E_g and T_g symmetry. Thus we write

$$H_e(\mathfrak{z}) = M_{1e}\mathfrak{z}^{-2} + M_{3e}\mathfrak{z}^{-4}\cdots\,, \tag{D13a}$$

$$M_t(\mathfrak{z}) = M_{1t}\mathfrak{z}^{-2} + M_{3t}\mathfrak{z}^{-4}\cdots\,, \tag{D13b}$$

where the subscripts denote the symmetry. Thus we have

$$M_{1e} = \tfrac{1}{2}\,\mathrm{Tr}\{\hat{\underline{D}}_e[\hat{\underline{A}}_e(\infty) + (\hat{\underline{M}}_{12}(\infty)\hat{\underline{R}})_e]\}\,, \tag{D14}$$

which we evaluate as

$$M_{1e} = \tfrac{8}{3}[E_0 + (5s_2 + 6s_6)(2\mathfrak{z}_0)^{-1}]\,. \tag{D15}$$

The explicit expressions for M_{1t}, M_{3e}, and M_{3t} are more complicated and will not be given here.

†Work supported in part by the National Science Foundation and the Advanced Research Projects Agency.

*Now at Department of Physics, University of California, Los Angeles, California.

[1]A. B. Harris, J. Appl. Phys. 42, 1574 (1971).

[2]R. G. Moorhouse, Proc. Phys. Soc. (London) 64A, 1097 (1951).

[3]G. G. Low, A. Okazaki, R. W. H. Stevenson, and K. C. Turberfield, J. Appl. Phys. 35, 998 (1964).

[4]R. Silberglitt and A. B. Harris, Phys. Rev. Letters 19, 30 (1967).

[5]E. J. Samuelsen, R. Silberglitt, G. Shirane, and J. P. Remeika, Phys. Rev. B 3, 157 (1971).

[6]H. deWijn, R. E. Walstedt, L. R. Walker, and H. J. Guggenheim, Phys. Rev. Letters 24, 832 (1970).

[7]P. A. Fleury, Phys. Rev. Letters 21, 151 (1968).

[8]R. J. Elliott, M. F. Thorpe, G. F. Imbusch, R. Loudon, and J. B. Parkinson, Phys. Rev. Letters 21, 147 (1968).

[9]R. J. Elliott and M. F. Thorpe, J. Phys. C 2, 1630 (1969).

[10]F. J. Dyson, Phys. Rev. 102, 1217 (1956); 102, 1230 (1956).

[11]C. F. Coll, III, A. B. Harris, and A. J. Berlinsky, Phys. Rev. Letters 25, 858 (1970).

[12]A. J. Berlinsky and A. B. Harris, following paper, Phys. Rev. B 4, 2808 (1971).

[13]T. Nakamura, Progr. Theoret. Phys. (Kyoto) 14, 135 (1955).

[14]H. P. Gush and J. Van Kranendonk, Can. J. Phys. 40, 1461 (1962).

[15]J. Van Kranendonk and G. Karl, Rev. Mod. Phys. 40, 531 (1968).

[16]P. Egelstaff, B. Heywood, and F. Webb, Proc. Phys. Soc. (London) 90, 681 (1967).

[17]A. B. Harris, L. I. Amstutz, H. Meyer, and S. M. Myers, Phys. Rev. 175, 603 (1968).

[18]W. Schott, Z. Physik 231, 243 (1970).

[19]R. W. Hill and B. W. A. Ricketson, Phil. Mag. 45, 277 (1954); B. W. A. Ricketson, Ph.D. thesis (Oxford University, 1954) (unpublished).

[20]G. Grenier and D. White, J. Chem. Phys. 40, 3015 (1964).

[21]A. J. Berlinsky and A. B. Harris, Phys. Rev. A 1, 878 (1970).

[22]J. F. Jarvis, H. Meyer, and D. Ramm, Phys. Rev. 178, 1461 (1969).

[23]D. Ramm, H. Meyer, J. F. Jarvis, and R. L. Mills, Solid State Commun. 6, 497 (1968); D. Ramm, H. Meyer, and R. L. Mills, Phys. Rev. B 1, 2763 (1970).

[24]F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953).

[25]J. R. Gaines, E. M. deCastro, and D. White, Phys. Rev. Letters 13, 425 (1964).

[26]L. I. Amstutz, H. Meyer, S. M. Meyers, and D. C. Rorer, Phys. Rev. 181, 589 (1969).

[27]B. Maraviglia, F. Weinhaus, H. Meyer, and R. L. Mills, Solid State Commun. 8, 815 (1970).

[28]A. B. Harris, Phys. Rev. B 2, 3495 (1970).

[29]F. Weinhaus, S. M. Myers, B. Maraviglia, and H. Meyer, Phys. Rev. B 3, 3730 (1971).

[30]J. H. Constable and J. R. Gaines, Phys. Rev. B 3, 1556 (1971).

[31]M. Bloom, Physica 23, 767 (1957).

[32]T. Moriya and K. Motizuki, Progr. Theoret. Phys. (Kyoto) 18, 183 (1957).

[33]W. P. A. Hass, G. Seidel, and N. J. Poulis, Physica 26, 834 (1960); W. P. A. Hass, N. J. Poulis, and J. J. W. Borleffs, Physica 27, 1037 (1961).

[34]M. J. Smith, D. White, and J. R. Gaines, J. Chem. Phys. 49, 3317 (1968).

[35]S. Homma, Progr. Theoret. Phys. (Kyoto) 40, 1 (1968); 43, 851 (1970).

[36]C. C. Sung, Phys. Rev. 167, 271 (1968).

[37]W. N. Hardy and J. R. Gaines, work cited in Ref. 36.

[38]L. I. Amstutz, H. Meyer, S. M. Myers, and R. L. Mills, J. Phys. Chem. Solids 30, 2693 (1969).

[39]F. Weinhaus, S. M. Myers, B. Maraviglia, and H. Meyer, Phys. Rev. B 3, 626 (1971).

[40]R. Wang, M. Smith, and D. White (unpublished).

[41]J. Hama and T. Nakamura, Progr. Theoret. Phys. (Kyoto) 44, 303 (1970).

[42]W. N. Hardy, I. F. Silvera, and J. P. McTague, Phys. Rev. Letters 22, 297 (1969).

[43]I. F. Silvera, W. N. Hardy, and J. P. McTague, Discussions Faraday Soc. 48, 54 (1969).

[44]S. Homma, K. Okada, and H. Matsuda, Progr. Theoret. Phys. (Kyoto) 36, 1310 (1966); 38, 767 (1967); 45, 330 (E) (1971).

[45]H. Ueyama and T. Matsubara, Progr. Theoret. Phys. (Kyoto) 36, 784 (1967).

[46]J. C. Raich and R. D. Etters, Phys. Rev. 168, 425 (1968).

[47]F. G. Mertens, W. Biem, and H. Hahn, Z. Physik 213, 33 (1968); 220, 1 (1969).

[48]A. J. Berlinsky, A. B. Harris, and C. F. Coll, III, Solid State Commun. 7, 1491 (1969).

[49]C. F. Coll, III and A. B. Harris, Phys. Rev. B 2, 1176 (1970).

[50]T. Nakamura and H. Miyagi, Progr. Theoret. Phys. (Kyoto) 44, 833 (1970).

[51]O. Nagai and T. Nakamura, Progr. Theoret. Phys. (Kyoto) 24, 432 (1960).

[52]H. M. James and J. C. Raich, Phys. Rev. 162, 649 (1967).

[53]R. J. Elliott, Discussions Faraday Soc. 48, 7 (1969).

[54]See F. Keffer, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, New York, 1966), Vol. XVIII/2.

[55]See L. R. Walker, in *Magnetism*, edited by G. Rado and H. Suhl (Academic, New York, 1963), Vol. I.

[56]S. V. Tyablikov, Ukr. Mat. Zh. 11, 287 (1959).

[57]F. Keffer and R. Loudon, J. Appl. Phys. 32, 25 (1961).

[58]T. Oguchi, Phys. Rev. 117, 117 (1956). Oguchi's results for the leading terms in the $1/S$ expansion are $U(0)=U_0(1+\frac{1}{2}c/S)$ and $\epsilon_{\mathbf{k}}=\epsilon_{\mathbf{k}}^0(1+c/S)$, where c is a constant. Thus, to this order in $1/S$ we have $(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}}^0)/\epsilon_{\mathbf{k}}^0=b[U(0)-U_0]/U_0$, where b is 2, rather than unity as suggested by Eq. (1.3).

[59]H. Horner, Phys. Rev. Letters 25, 147 (1970).

[60]A. B. Harris, Phys. Rev. Letters 21, 602 (1968).

[61]J. Steward, J. Phys. Chem. Solids 1, 1946 (1956); H. Megaw, Phil. Mag. 28, 129 (1939).

[62]A. B. Harris, Intern. J. Quantum Chem. IIS, 347 (1968).

[63]J. Noolandi and J. VanKranendonk, Phys. Letters 30A, 258 (1969).

[64]A. B. Harris, Phys. Rev. B 1, 1881 (1970).

[65]Clustering effects have been detected in H_2 at low temperatures, but up to now only for low $(J=1)$ concentrations. See Ref. 22 and also L. I. Amstutz, J. R. Thomp-

son, and H. Meyer, Phys. Rev. Letters 21, 1175 (1968). See also Ref. 88, below.

[66]R. L. Mills and A. F. Schuch, Phys. Rev. Letters 15, 722 (1965); A. F. Schuch and R. L. Mills, *ibid.* 16, 616 (1966).

[67]K. F. Mucker, S. Talhouk, P. M. Harris, and D. White, Phys. Rev. Letters 15, 586 (1965); K. F. Mucker, S. Talhouk, P. M. Harris, D. White, and R. A. Erickson, *ibid.* 16, 799 (1966); K. F. Mucker, P. M. Harris, D. White, and R. A. Erickson, J. Chem. Phys. 49, 1922 (1968).

[68]L. Wolniewicz, J. Chem. Phys. 45, 515 (1966); G. Karl and J. D. Poll, J. Chem. Phys. 46, 2944 (1967).

[69]M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[70]S. V. Maléev, Zh. Eksperim. i Teor. Fiz. 33, 1010 (1956) [Sov. Phys. JETP 6, 776 (1956)].

[71]A. B. Harris, J. Phys. Chem. Solids 27, 1927 (1966).

[72]C. Bloch and C. de Dominicis, Nucl. Phys. 7, 459 (1958).

[73]R. Balian and C. de Dominicis, Compt. Rend. 250, 3285 (1960).

[74]A. A. Abrikosov, L. P. Gor'kov, and I. Y. Dzyaloshinskii, *Quantum Field Theoretical Methods in Statistical Physics*, 2nd ed. (Pergamon, New York, 1965).

[75]We set $\hbar = 1$.

[76]This point of view is similar to that of the theory of quantum crystals as developed by L. H. Nosanow and N. R. Werthamer [Phys. Rev. Letters 15, 618 (1965)].

[77]Y. Nambu, Phys. Rev. 117, 648 (1960).

[78]G. Baym and N. D. Mermin, J. Math. Phys. 2, 232 (1961).

[79]Physical properties, such as the libron energies, are determined by the analytic continuation of the Green's function to $\mathfrak{z} = \omega \pm i0^{\pm}$. In our case the analytic continuation is accomplished by replacing $\mathfrak{z}_r$ by $\mathfrak{z}$ and is unique, as is shown in Ref. 78.

[80]It is not commonly recognized that the average harmonic libron energy is *not* E_0, but is $E_0 + \Delta E^{(2)}$.

[81]Max Born and Kun Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954), p. 203.

[82]L. Van Hove, Phys. Rev. 95, 249 (1954).

[83]I. Silvera (private communication).

[84]G. Meissner, Phys. Rev. Letters 21, 435 (1968).

[85]This argument was suggested to us by H. Meyer.

[86]Actually, since Ramm *et al.* used a harmonic density of states, their calculation takes proper account of the term $\Delta E^{(2)}$ in Eq. (4.2). Hence their libron energy Δ should really be identified with $E_L - \Delta E^{(2)}$ and not with E_L.

[87]I. F. Silvera, W. N. Hardy, and J. P. McTague, Bull. Am. Phys. Soc. 15, 1662 (1970).

[88]R. J. Roberts and J. G. Daunt, Phys. Letters 33A, 353 (1970).

[89]R. J. Elliott and W. M. Hartmann, Proc. Phys. Soc. (London) 90, 671 (1967).

[90]H. Miyagi and T. Nakamura, Progr. Theoret. Phys. (Kyoto) 37, 641 (1967).

[91]H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Natl. Bur. Std. (U. S.) 41, 379 (1948).

[92]A. Bellemans and A. Babloyantz, Mol. Phys. 2, 169 (1959).

[93]W. Meckstroth and D. White, J. Chem. Phys. 54, 3723 (1971).

[94]S. H. Walmsley and J. A. Pople, Mol. Phys. 8, 345 (1964).

[95]In Ref. 48 the coordinate system and notation used were different, so that $x_0 = 19\Gamma x^*$, where x is the value from Ref. 48.

[96]E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic, New York, 1959), p. 75.