which are quite similar to the shell model have been discussed in detail.[1,2]

The crystal structure of Mg_2Sn is the same as CaF_2. (See Fig. 6.) The lattice is face-centered cubic and the basis consists of a Sn ion at the origin and Mg ions at $(a/4, a/4, a/4)$ and at $(\frac{3}{4}a, \frac{3}{4}a, \frac{3}{4}a)$, a is the lattice constant. The Sn ions occupy centers of inversion symmetry, but Mg ions do not.

The lattice vibration frequencies are roots of the secular equation

$$|m_k\omega^2\delta_{kk'}\delta_{\alpha\beta}+[{}^{kk'}_{\alpha\beta}]| = 0, \tag{1}$$

where $k = 1$ for the Sn core, $k = 1'$ for the Sn shell, and $k = 2$ and 4 for the Mg ions. α and β index the coordinates x, y, and z. The coupling coefficients $[{}^{kk'}_{\alpha\beta}]$ are written as the sum of the short range and Coulomb coupling coefficients, $S[{}^{kk'}_{\alpha\beta}]$ and $C[{}^{kk'}_{\alpha\beta}]$. The Coulomb terms have been tabulated by KELLERMAN[23] and by WHITTEN *et al.*[1] for 47 points in the Brillouin zone. The only difference between $C[{}^{1k}_{\alpha\beta}]$ and $C[{}^{1k'}_{\alpha\beta}]$ is the charge multiplying the coefficient.

We list below the expression of GANESAN and SRINIVASAN[24] for the short range coupling coefficients with appropriate changes for our shell model.

$$S[{}^{11}_{\alpha\alpha}] = -8\alpha_1-4\alpha_2-8\beta_2+4\alpha_2\cos\frac{a}{2}q_\beta\cos\frac{a}{2}q_\gamma$$
$$+4\beta_2\cos\frac{a}{2}q_\alpha\left(\cos\frac{a}{2}q_\beta+\cos\frac{a}{2}q_\gamma\right)-\delta, \tag{2}$$

$$S[{}^{11}_{\alpha\beta}] = 4\gamma_2\sin\frac{a}{2}q_\alpha\sin\frac{a}{2}q_\beta,$$
$$S[{}^{11'}_{\alpha\alpha}] = \delta,$$
$$S[{}^{11'}_{\alpha\alpha}] = 0,$$
$$S[{}^{12}_{\alpha\alpha}] = \alpha_1[\exp[i(a/4)(q_\alpha+q_\beta+q_\gamma)]$$
$$+\exp[i(a/4)(q_\alpha-q_\beta-q_\gamma)]$$
$$+\exp[i(a/4)(-q_\alpha+q_\beta-q_\gamma)]$$
$$+\exp[i(a/4)(-q_\alpha-q_\beta+q_\gamma)]],$$
$$S[{}^{12}_{\alpha\beta}] = \beta_1[\exp[i(a/4)(q_\alpha+q_\beta+q_\gamma)]$$
$$-\exp[i(a/4)(q_\alpha-q_\beta-q_\gamma)]$$
$$-\exp[i(a/4)(-q_\alpha+q_\beta-q_\gamma)]$$
$$+\exp[i(a/4)(-q_\alpha-q_\beta+q_\gamma)]],$$
$$S[{}^{1'2}_{\alpha\alpha}] = 0,$$
$$S[{}^{1'2}_{\alpha\beta}] = 0,$$
$$S[{}^{1'4}_{\alpha\alpha}] = 0,$$
$$S[{}^{1'4}_{\alpha\beta}] = 0,$$
$$S[{}^{22}_{\alpha\alpha}] = -4\alpha_1-2\alpha_3-4\beta_3,$$
$$S[{}^{22}_{\alpha\beta}] = 0,$$
$$S[{}^{24}_{\alpha\alpha}] = 2\beta_3\left(\cos\frac{a}{2}q_\beta+\cos\frac{a}{2}q_\gamma\right)+2\alpha_3\cos\frac{a}{2}q_\alpha,$$
$$S[{}^{24}_{\alpha\alpha}] = 0,$$

where $\alpha \neq \beta$ and a is the lattice constant. The remaining coefficients can be obtained by the relations

$$S[{}^{kk'}_{\alpha\beta}] = S[{}^{k'k}_{\beta\alpha}]^*,$$
$$S[{}^{14}_{\alpha\beta}] = S[{}^{12}_{\alpha\beta}]^*. \tag{3}$$

The subscripts 1, 2, and 3 on the force constants correspond to Mg–Sn, Sn–Sn, and Mg–Mg forces, respectively. δ is the force constant associated with the Sn core–Sn shell interaction. (See the appendix for exact definitions of force constants.)

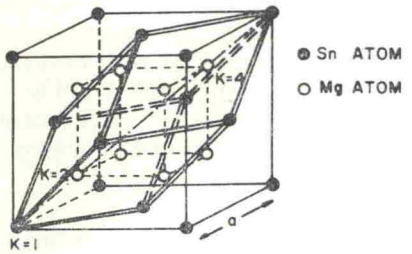

FIG. 6. The crystal structure of Mg_2Sn. The position vectors of the basis in the unit cell are given by $r_k = a/4(k-1)[1, 1, 1]$.

In the limit of long wavelengths ($q = 0$), we have as roots of the secular equation:

$$\omega_A{}^2 = 0,$$
$$\omega_R{}^2 = \frac{4}{m_2}(\alpha_1+\alpha_2+2\beta_3),$$
$$\omega_I{}^2 = \left(\frac{2}{m_1}+\frac{1}{m_2}\right)\left(4\alpha_1-2C\frac{e_2{}^2}{V\left(1-\frac{4\pi}{3V}\alpha\right)}\right), \tag{4}$$

where C has the value $4\pi/3$ for transverse modes, $-8\pi/3$ for the longitudinal mode, e_2 is the charge on the Mg ions and in our shell model is equivalent to the SZIGETI[25,26] charge, V is the volume of a primitive cell, $a^3/4$, and $\alpha = e_1'^2/\delta$ is the atomic polarizability of the Sn ion (where e_1' is the charge on the Sn shell). α is related to the high frequency dielectric constant by

$$\frac{4\pi}{3V}\alpha = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}. \tag{5}$$

For Mg_2Sn, we found $(4\pi/3V)\alpha = 0{\cdot}829$. In the point ion models, the expressions for the frequencies do not contain the $(4\pi/3V)\alpha$ term because the polarizability was neglected.

At the zone center, the acoustic modes, ω_A, and the Raman modes, ω_R, are triply degenerate, while the transverse infrared mode, ω_{IT}, is doubly degenerate, and the longitudinal infrared mode, ω_{IL}, is non-degenerate. Since ω_{IT} and ω_{IL} are known experimentally, the third expression in equation (4) can be used to evaluate α_1 and e_2. (For numerical values of the shell model and the point ion models, see Table 2.) The Raman frequency is not known, so no information is gained from the second expression in equation (4).

Table 2. Force constants (in units of 10^4 dyn/cm) *and* Mg *ion charge (in units of* 10^{-10} e.s.u.) *for various models*

	α_1	β_1	α_2	β_2	α_3	β_3	e_2
Model I	1·033	0·841	0	0·456	0·599	0	2·397
Model II	1·033	1·310	0·412	0·755	0	0	2·397
Shell model	1·290	1·365	0·356	0·567	0·250	0	1·630

The subscripts 1, 2 and 3 on the force constants correspond to Mg–Sn, Sn–Sn, and Mg–Mg forces respectively.

The polarization of the Sn ions will not affect the elastic constants since the Sn ions are at points of inversion symmetry. Therefore, we could take over the expressions given by CHUNG *et al.*[2] for the point ion models:

$$C_{11} = \frac{2}{a}\left(\alpha_1 + 2\beta_2 + \alpha_3 + 3{\cdot}276\frac{e_2^2}{V}\right),$$

$$C_{12} = \frac{2}{a}\left(2\beta_1 - 2\gamma_2 - \alpha_1 - \alpha_2 - \beta_2 - \beta_3 - 5{\cdot}395\frac{e_2^2}{V}\right), \tag{6}$$

$$C_{44} = \frac{2}{a}\left(\alpha_1 + \alpha_2 + \beta_2 + \beta_3 - 1{\cdot}527\frac{e_2^2}{V} - \frac{\left(-\beta_1 + 5{\cdot}038\frac{e_2^2}{V}\right)^2}{\alpha_1 + \alpha_3 + 2\beta_3}\right).$$

Following CHUNG *et al.*[2], we eliminated a disposable parameter by imposing axial symmetry about the line joining the two Sn ions, so that $\alpha_2 = \beta_2 + \gamma_2$. But equations (4), (5) and (6) did not uniquely define all the parameters in our shell model. In particular, equation (5) only determined the ratio $e_1'^2/\delta$. Therefore, we picked a value of $+4|e|$ for the charge on the Sn core. Since the Mg ion charge, e_2, was determined by equation (4), e_1 was determined by the condition of charge neutrality in a cell

$$e_1 + e_1' + 2e_2 = 0. \tag{7}$$

The results of our calculation were rather insensitive to the value that we picked for the core charge. Finally, we chose $\beta_3 = 0$ for simplicity (it corresponds to a non-central Mg–Mg force) and $\alpha_3 = 0{\cdot}250 \times 10^4$ dyn/cm to give a reasonable fit to the specific heat data. α_3 is the central Mg–Mg force constant. The remaining parameters were then evaluated from equations (4), (5) and (6).

RESULTS OF THE CALCULATIONS

The roots of the secular equation (1) were solved numerically at the 47 points in $\frac{1}{48}$ of the Brillouin zone chosen by KELLERMAN[23] with an IBM 360-50 computer. The reduced specific heat, $Cv/9R$, where R is the universal gas constant, was calculated from the expression

$$\frac{C_v}{9R} = \frac{\sum E\left(\frac{\hbar\omega}{kT}\right) w(q)}{9\sum w(q)},$$