Raman Scattering in Mg_2Si, Mg_2Ge, and Mg_2Sn†

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The one-phonon Raman scattering of Mg_2Si, Mg_2Ge, and Mg_2Sn at room, dry-ice, and liquid-nitrogen temperatures is reported. The Raman frequencies obtained ($\Gamma_{25'}$ optical phonon) decrease with increasing temperature. The room-temperature results for Mg_2Sn are in excellent agreement with recent neutron-scattering data; such data are not available for Mg_2Ge and Mg_2Si. In these cases, the Raman frequencies obtained are compared with lattice-dynamical calculations based on the reststrahlung frequencies and the elastic constants. The Raman lines observed show considerable sharpening (a factor of 2 to 3) between room and liquid-nitrogen temperature. Weaker, possibly two-phonon, spectra have also been observed.

INTRODUCTION

Mg_2Si, Mg_2Ge, and Mg_2Sn are cubic semiconductors which crystallize in the antifluorite structure with a face-centered cubic lattice. The average number of valence electrons per atom is four, and thus their electronic structure is closely related to that of the germanium, zinc-blende and wurtzite materials, and to the alkali halides.[1] This similarity is exhibited rather closely in the band structures[2,3] and, correspondingly, in the electronic optical properties of Mg_2Si, Mg_2Ge, and Mg_2Sn.[4–6]

While similarities exist between the band structures of Mg_2X and of the germanium-zinc-blende-type materials, their lattice-vibrations spectra are considerably different. Mg_2X can be considered as a zinc-blende-type material, with the cations which would be at $\frac{1}{4}a_0$ (1, 1, 1) replaced by two magnesium atoms at $\frac{1}{4}a_0$ (1, 1, 1) and at $\frac{1}{4}3a_0$ (1, 1, 1), respectively. Thus, the materials have three atoms in the primitive unit cell, and inversion symmetry is recovered. The presence of three atoms per unit cell produces two sets of optical branches. The existence of inversion symmetry makes these branches either infrared active (odd parity, Γ_{15}) or optically active (even parity, $\Gamma_{25'}$) at $\vec{k}=0$. The infrared-active branches are split by the macroscopic Coulomb field into LO and TO phonons, their frequencies obeying the Lyddane-Sachs-Teller relation. No such splitting occurs for the $\Gamma_{25'}$ branches.

The infrared-active Γ_{15} modes have been the object of considerable work.[7,8] On the basis of the determined longitudinal and transverse frequencies ν_{LO} and ν_{TO}, and the measured elastic constants, force-constant models for the phonon spectra of Mg_2Si and Mg_2Ge have been constructed.[9,10] These models predict a Raman frequency ν_R which varies considerably depending on the assumptions made for the force constants. In this work, we report direct measurements of the Raman frequencies for Mg_2Si and Mg_2Ge, at room, dry-ice, and pumped-liquid-nitrogen temperatures (~64 °K), and for Mg_2Sn at room temperature and at 64 °K. The results for Mg_2Sn are in excellent agreement with recent neutron-scattering measurements.[11] A temperature dependence of these phonon frequencies and of the linewidths has been observed. The results are compared with recent work on the temperature dependence of the one-phonon Raman line in silicon.[12]

EXPERIMENT

Our measurements were performed with the 4880-Å line of a $\frac{1}{2}$-W argon-ion laser (Coherent Radiation, model No. 54). Since all materials under discussion are opaque to this wavelength, the measurements were performed in the backscattering configuration. A Jarrell-Ash 1-m monochromator, with detection by photon counting, was used. The wavelengths of the phonon-shifted lines were determined by comparison with several reference lines of a neon low-pressure lamp.

The measurements were performed on [111] surfaces of cleavage of single crystals. Care was taken to reduce contact with humid air to a minimum, especially for the highly hygroscopic Mg_2Ge samples. The scattering surface was nearly parallel to the entrance slit while the laser beam was kept at an angle of 30° with the normal to that surface. The polarization selection rules associated with this configuration were checked and found to correspond to the $\Gamma_{25'}$ component of the Raman tensor for the one-phonon lines. Only Stokes scattering was studied.

The low-temperature measurements were performed with the samples immersed in either pumped liquid nitrogen (to avoid bubbles) or in methanol, cooled with dry ice (with pieces of dry ice only above the sample to avoid bubbles). The temperature was monitored with a copper-constantan thermocouple placed near the sample. The temperature stability was better than ±1 °C. The absence of bubbles at the sample surface when the laser beam

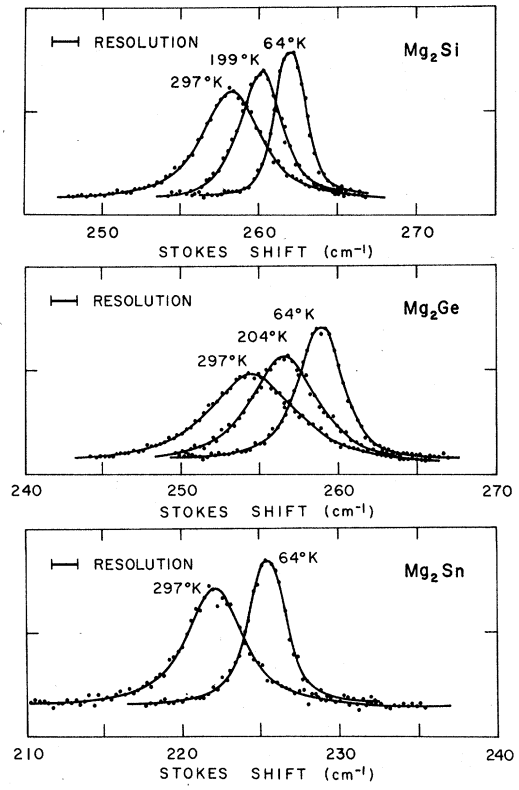

FIG. 1. One-phonon Stokes-Raman spectra of Mg_2Si, Mg_2Ge, and Mg_2Sn at several temperatures. Vertical scale is in arbitrary units.

is applied indicates a negligible amount of surface heating by the laser. From estimated values of thermal conductivity, specific heat, and incident laser-power density (200 W cm^{-2}) we estimate the temperature rise in vacuum would not exceed 10 °C. For Mg_2Sn no data were obtained at dry-ice temperature: The small scattering cross section for this material together with the large scattering of the turbulent methanol made measurements at this temperature unreliable.

RESULTS AND DISCUSSION

The one-phonon Stokes-Raman scattering spectra observed by Mg_2Si, Mg_2Ge, and Mg_2Sn are shown in Fig. 1. The frequencies observed at the various experimental temperatures are shown in Table I, together with the measured half-power linewidths W (uncorrected). The linewidths observed at the lowest temperatures are of the order of the instrumental resolution for the 50-μ entrance slit used ($W_i = 1.7$ cm^{-1} measured with the laser line). We therefore also list in Table I the linewidths corrected with the expression obtained under the assumption of Gaussian line shapes and slit functions;

$$W(\text{uncorrected}) = [W(\text{corrected})^2 + W_i^2]^{1/2}. \quad (1)$$

In view of the fact that the observed line shapes and slit functions are not exactly Gaussian, Eq. (1) is to be viewed only as an approximation.

The Stokes-Raman spectra of Mg_2Si, Mg_2Ge, and Mg_2Sn over a broader spectra region at 297 °K are shown in Fig. 2 with an expanded vertical scale. These spectra were taken without an analyzer and, for our [111] surfaces, they were approximately independent of the polarization of the incident light. The corresponding spectra obtained with crossed polarizer and analyzer were reduced in intensity by at least an order of magnitude. The structure at about $2\nu_R$ observed for Mg_2Sn and Mg_2Ge is likely to be second-order, two-phonon scattering: The longitudinal branch of the $\Gamma_{25'}$ phonon curves is quite flat[9-11] and should give two-phonon structure near $2\nu_R$. This branch is curved upwards at $\vec{k}=0$ and hence the center of mass of the corresponding two-phonon line is expected to be slightly above $2\nu_R$, in agreement with Fig. 2. We should point out that the two-phonon spectra of Mg_2Ge and Mg_2Sn shown in Fig. 2 are very similar to the two-phonon spectrum observed by Parker *et al.* for silicon.[13]

The weak lines in the spectrum of Mg_2Si shown in Fig. 2, however, are quite different from those for Mg_2Ge and Mg_2Sn. In fact, it is not possible to interpret these lines as two-phonon scattering. The line at 690 cm^{-1} has a characteristic one-dimensional critical point shape $[(\nu_g - \nu)^{-1/2}]$ and a frequency roughly twice that of the weaker structure at 345 cm^{-1}. These lines could possibly be due to

TABLE I. Frequencies and linewidths observed for the one-phonon Stokes line of Mg_2Si, Mg_2Ge, and Mg_2Sn. Dry-ice data at 199 °K for Mg_2Si and 204 °K for Mg_2Ge. Estimated error in ν_R and W(uncorrected) is ±0.2 cm^{-1}. All data are in cm^{-1}, also lattice constants a_0 are at room temperature.

	ν_R (cm^{-1})			W(uncorrected) (cm^{-1})			W(corrected) (cm^{-1})			a_0[a] (Å)
	64 °K	Dry ice	297 °K	64 °K	Dry ice	297 °K	64 °K	Dry ice	297 °K	297 °K
Mg_2Si	262.0	260.1	258.3	2.3	3.2	4.4	1.65	2.7	4.0	6.338
Mg_2Ge	259.8	256.6	254.5	3.35	4.9	6.5	2.9	4.6	6.3	6.393
Mg_2Sn	225.5	• • •	222.1	2.9	• • •	4.3	2.3	• • •	3.9	6.762

[a]J. M. Eldridge, E. Miller, and K. L. Komarek, Trans. Met. Soc. AIME 239, 775 (1967).

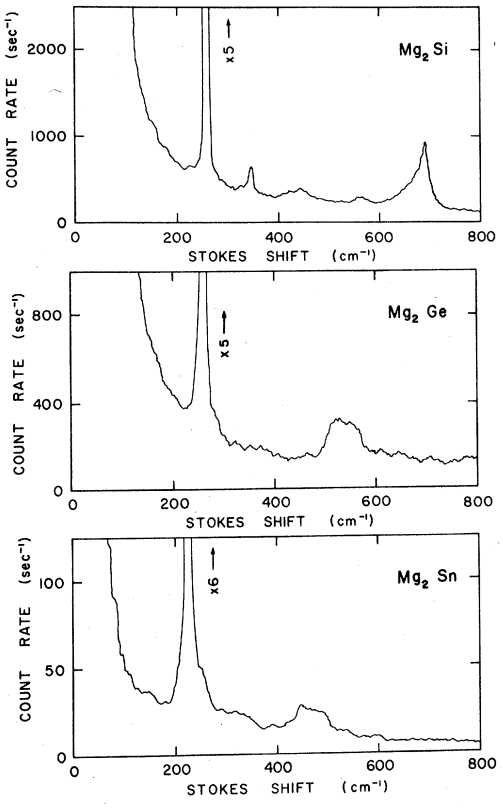

FIG. 2. Stokes-Raman spectra of Mg_2Si, Mg_2Ge, and Mg_2Sn at room temperature over a broad spectral range.

some surface layer of a different composition: It has been suggested[14] that the relative stability of Mg_2Si in moist air is due to the formation of an oxide layer on its surface.

We did not find in the literature values for the linear expansion coefficient of the compounds under study. A comparison of their Debye temperatures[9,11] with those of the germanium-type compounds suggests that the linear expansion coefficient of our Mg_2X compounds should be around 4×10^{-6} $(°C)^{-1}$, increasing slightly with average atomic number. Hence, the fractional change in Raman frequency with temperature shown in Table I is about five times larger than the corresponding change in volume due to thermal expansion. This result is similar to that found for Si [12] and for α-Sn, [15] and indicates that the component of the frequency shift with temperature produced by thermal expansion is negligible (the hydrostatic Grüneisen constant[15] is expected to be close to 1).

In the Raman-active $\Gamma_{25'}$ mode of Mg_2X, the magnesium atoms vibrate in opposite directions, while X remains stationary. The variation of ν_R with X shown in Table I can be used to study the dependence of the restoring forces on lattice constant. It has been shown[15,16] that throughout the sequence Si, Ge, α-Sn, ν_R varies like $a_0^{-3/2}$. However, when one given material of this series is compressed hydrostatically, ν_R varies like a_0^{-3}, the difference being attributed to hard-core effects.[15] One may argue that since throughout the sequence Mg_2X one is only replacing one-third of the atoms, the Raman frequency should go like a_0^{-n}, with n a weighted average of 3 (hydrostatic case, weight 2) and 1.5 (Si–Ge–α-Sn case, weight 1). Thus, we would expect $n=2.5$. The results of Table I for a given temperature can be fitted well with $\nu_R \propto a_0^{-2.4}$. In view of this fact, measurements of the dependence of ν_R on hydrostatic stress would be very interesting.

TABLE II. Raman and infrared frequencies, and width of the reststrahlen peak W_{TO} obtained by other workers for Mg_2Si, Mg_2Ge, and Mg_2Sn.

	ν_R (cm^{-1})	ν_{TO} (cm^{-1})	ν_{LO} (cm^{-1})	W_{TO} (cm^{-1})
Mg_2Si (300 °K)	258[a]	267[b]	327[b]	
Mg_2Ge (300 °K)	265[c]	207[b]	237[b]	
Mg_2Sn (300 °K)	222.3[d]	189[e]	232[e]	7[e]
Mg_2Sn (100 °K)		193[e]	232[e]	5[e]

[a]Reference 9.
[b]Reference 7.
[c]Reference 10.
[d]Reference 11.
[e]Reference 8.

We have listed in Table II values of ν_R obtained by other authors, together with the corresponding values of the reststrahlung frequencies ν_{TO} and ν_{LO}. The agreement between our results for ν_R and those

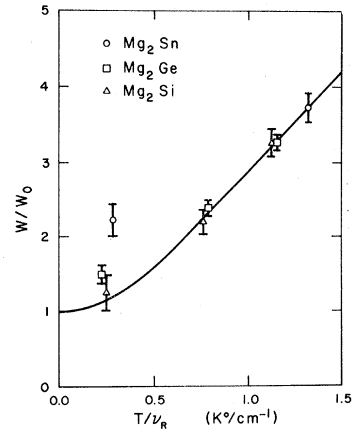

FIG. 3. Temperature dependence of the corrected linewidths of the one-phonon Stokes line of Mg_2Si, Mg_2Ge, and Mg_2Sn; also line predicted with Eq. (2). For convenience, the abcissa T/ν_R is given in °K/cm^{-1}.

obtained by neutron scattering[11] is excellent. The force-constant model of Chung *et al.*[10] for Mg_2Ge and of Whitten *et al.*[9] for Mg_2Si gives values of ν_R in good agreement with our measurements.

It has been suggested[12] that the linewidth W of the one-phonon line is determined mostly by decay into two phonons of roughly the same energy, and hence its temperature dependence is given by

$$W(T) = W(0)\{1 + 2/[\exp(h\nu_R/2kT) - 1]\}. \quad (2)$$

Figure 3 shows the corrected linewidths of Table I as a function of T/ν_R and the curve of Eq. (2). This curve represents well the experimental temperature dependence of W for Mg_2Si and, in view of the uncertainties in the correction of Eq. (1), for Mg_2Ge as well. For Mg_2Sn, Fig. 3 suggests some additional temperature-independent broadening mechanism. The same conclusion can be drawn from the temperature dependence of the restrahlung linewidth of Mg_2Sn, shown in Table II.

Note added in proof. We have measured the dependence of the one-phonon Raman line of Mg_2Sn on hydrostatic stress and we have found the corresponding Gruneisen constant to be close to 1, in agreement with the conjecture made in the discussion. Raman data for these materials and for Mg_2Pb have been also presented recently by Anastassakis and Perry [Bull. Am. Phys. Soc. 16, 29 (1971)].

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Dopant Diffusion in Silicon. III. Acceptors

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Aluminum, gallium, indium, and thallium acceptors have been diffused into (111) silicon from doped epitaxially deposited source layers in a flowing hydrogen atmosphere. As in the case of P, As, Sb, and Bi donors reported earlier, all these acceptors show significantly lower mobilities when freed from surface effects. The temperature dependence of the intrinsic diffusion coefficients, obtained above 1120 °C, are characterized by the following preexponential and activation-energy parameters: 1.385, 0.374, 0.785, (1.37) cm^2/sec, and 3.41, 3.39, 3.63, (3.70) eV/atom for Al, Ga, In, Tl, respectively. An analysis of these diffusion characteristics indicate a similar point-defect mechanism for both group-III and group-V dopants in silicon.

I. INTRODUCTION

This is the third in a series of papers dealing with the intrinsic diffusion of group-III and group-V dopants in silicon.[1,2] All the group-V donors were found to migrate by a closely coupled donor-vacancy pair.[2] On the other hand, the diffusion behavior of the boron acceptor was found to be very