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Linewidth behavior of the A_{1g} Raman phonon in $Cd_xHg_{1-x}I_2$ solid solution

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The behavior of the A_{1g} phonon line in $Cd_xHg_{1-x}I_2$ (with $0<x<0.38$) solid solution has been investigated by Raman spectroscopy between 20 and 300 K. At room temperature, the A_{1g} linewidth unexpectedly decreases as the cadmium concentration is increased; at low temperature, the more conventional opposite trend is observed. By taking into account a variation of the final density of states in which the A_{1g} phonon decays, a convincing explanation of the experimental results is given. In addition, useful information on the behavior of the boundary LO(X) and/or LA(X) phonons in the solid solution can be extracted.

INTRODUCTION

In spite of the large amount of work already done, many aspects of the lattice vibrations in solid solutions are still questionable and their investigation is an open field of research[1-5] at the present time. Raman spectroscopy is known to be one of the most powerful and used techniques for studying phonons in solids; however, when mixed compounds are investigated, the interpretation of the experimental results very often becomes difficult.

First of all, the symmetry reduction of the pure-compound space group is difficult to deal with.[3] For example, the lack of translational symmetry may imply a relaxation of the K-selection rule.[1] Therefore some vibrations with finite wave vector become Raman active in the perturbed crystal. It turns out that the broadening of Raman phonons in solid solutions is often related to this inhomogeneous contribution. Moreover, the change of the homogeneous broadening (and therefore of the phonon lifetime) due to alloying should also be considered.[2,5]

In general both homogeneous and inhomogeneous broadenings have to be taken into account in order to explain the phonon linewidths. Since they come from different physical mechanisms, various experimental approaches are necessary to evaluate their relative strength.[5]

In this work, we have investigated the microscopic origin of the A_{1g} phonon spectral broadening in the system $Cd_xHg_{1-x}I_2$ as a function of composition ($0<x<0.38$) and temperature (20–300 K) by means of Raman spectroscopy. We show that the temperature behavior of the phonon linewidth allows evaluation of the homogeneous and inhomogeneous contribution to the phonon spectral broadening. Further, this kind of investigation gives fundamental information on the phonon decay processes and therefore on the phonon lifetime.

RESULTS AND DISCUSSION

In previous papers,[6] the interpretation of the Raman spectra for this system as well as some peculiar features of the mercuric iodide anharmonicity has been presented. Single-crystal characterization as well as details of the experimental apparatus presently used can also be found in these works. For x between 0 and 0.44, the system $Cd_xHg_{1-x}I_2$ belongs to D_{4h}^{15} ($P4_2/nmc$) space group; single crystals are laminar semiconductors with irreducible representation of the lattice vibrations at $K=0$ as follows:[6]

$$\underline{\Gamma}=A_{1g}+2A_{2u}+B_{2u}+2B_{1g}+3E_g+3E_u\ . \tag{1}$$

We turn our attention to A_{1g} normal mode of vibration in which the cation (Hg or Cd) mass does not oscillate, while the two anions (iodine) vibrate one against the other.[6] The experimental spectra taken at room temperature for $x=0,0.23,0.38$ are reported in Fig. 1. The most interesting aspect is the narrowing of the phonon linewidth as alloying takes place. Figure 2 shows the full widths at half maximum (Γ) as a function of composition with temperature ranging from 50 to 300 K. The instrumental spectral bandpass has been accounted for in evaluating the phonon linewidth. In the high-temperature range (200–300 K), Γ surprisingly decreases as the cadmium concentration increases; at lower temperatures the usual trend of the disordered systems is observed.

In solid solutions the breakdown of the K-selection rule induces a broadening of the Raman lines with a maximum for concentration values close to the central composition. Figure 2 shows that this effect is completely inadequate in order to explain the experimental behavior. As we will see later, present data rather suggest that cadmium content strongly influences the decay processes.

In mercuric iodide the A_{1g} phonon at $\Omega=114\ \text{cm}^{-1}$ decays in three phonons belonging to the X point of the Brillouin zone.[7] In fact the occurrence of an energy gap in the phonon density of states[8] prevents the decay of the A_{1g} mode into two phonons of lower frequency because of energy conservation. Following Ref. 9, the full width Γ can be written as

$$\Gamma=a+b[n(\Omega/2)+\tfrac{1}{2}]+c\{[n(\Omega/3)+\tfrac{1}{2}]^2+\tfrac{1}{12}\} \tag{2}$$

which depends on temperature through the Bose-Einstein factors $n(\Omega/2)$ and $n(\Omega/3)$; a, b, and c are positive constants. In Eq. (2) the first term takes into account scattering processes due to defects or impurities which are tem-

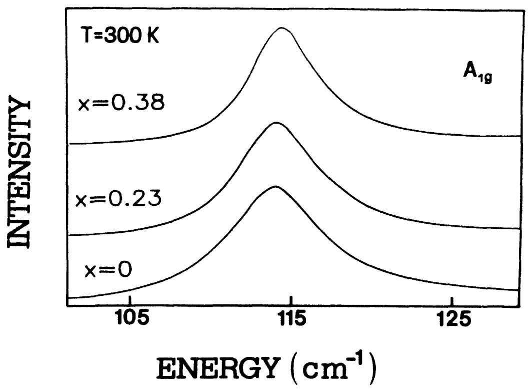

FIG. 1. Room-temperature spectra of the A_{1g} mode in $Cd_xHg_{1-x}I_2$ ($x=0$, 0.23, and 0.38).

perature independent. The second one (cubic anharmonicity) is related to events in which the A_{1g} phonon decays into two vibrational modes with frequency equal to $\frac{1}{2}\Omega(A_{1g})$. Since $n(\Omega)$ is the Bose-Einstein factor, this term behaves linearly with temperature. The last one (quartic anharmonicity) describes decays into three phonons with frequency $\frac{1}{3}\Omega(A_{1g})$ and it depends quadratically on temperature.

In order to estimate the parameters a, b, and c which are, indeed, proportional to the efficiency of each decay channel, a least-squares fit of the experimental data with Eq. (2) has been performed. The results for three different compositions are reported in Table I. It is worthwhile to notice that the constant a is always negligible. This implies that no contribution from disorder-allowed phonons close to the Γ point is present also in the mixed crystals. On the other hand, this is in agreement with the nature of the A_{1g} normal mode. In this vibration the cation mass does not move, while the iodine anions vibrate one against the other. Therefore no mass disorder is introduced in the alloys. In addition the force fluctuations should also be very small, since the frequency shift of this mode was found negligible in the solid solution.[6]

In the mixed crystals the cubic anharmonicity increases with cadmium concentration while the opposite trend is observed for the three-phonon decay process. These contributions to the full phonon linewidth are reported in Fig. 3 by solid lines. The points represent the experimental data.

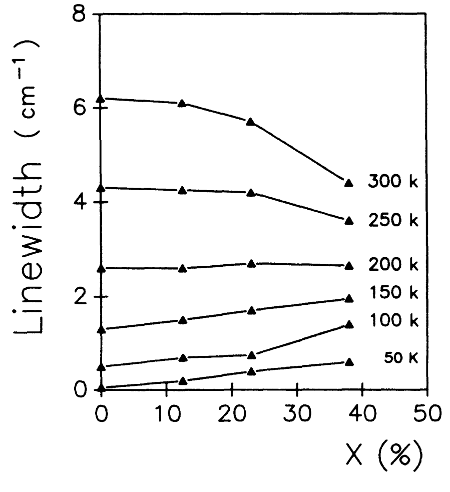

FIG. 2. A_{1g} linewidth behavior as a function of cadmium concentration for temperatures between 50 and 300 K. The straight lines are only a guide to follow the experimental data behavior.

TABLE I. a, b, and c parameters obtained from the best fits of the experimental data with Eq. (1). a describes the temperature-independent contribution to the linewidth, while b and c are related to the cubic and quartic anharmonicity, respectively.

$Cd_xHg_{1-x}I_2$	$x=0$	$x=0.23$	$x=0.38$
a (cm^{-1})	0.1	0.1	0.1
b (cm^{-1})	0.01	0.23	0.80
c (cm^{-1})	0.21	0.16	0.06

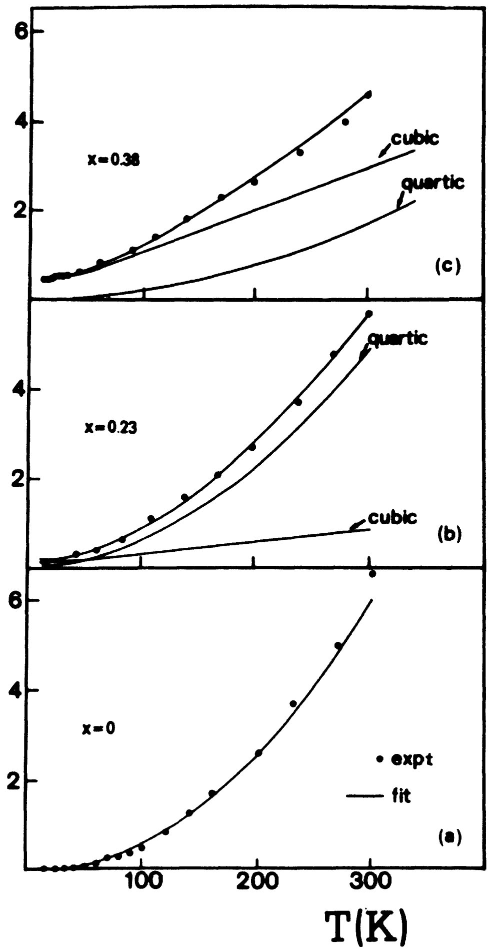

FIG. 3. A_{1g} linewidth behavior as a function of temperature for three different cadmium concentrations. The cubic and quartic anharmonic contributions are found by means of Eq. (2) in the text.

In mercuric iodide ($x=0$) only the c factor is different from zero and, as expected, only the three-phonon relaxation process occurs. The more effective decay mode of the A_{1g} phonon is the creation of three longitudinal-optical and/or longitudinal-acoustical (LO-LA) phonons of 39 cm^{-1} belonging to the X point of the Brillouin zone.[8] Every other possibility is ruled out by energy considerations. In the mixed crystals ($x>0$) the contribution of the term linear in temperature indicates that the phonon density of states at $\frac{1}{2}\Omega(A_{1g})$ has a finite value which increases with cadmium concentration. Though the phonon dispersion curves of the mixed compounds are missing, a possible explanation of the origin of this alternative decay channel can be given.

In solid solutions phonon resonances can follow a one- or a two-mode behavior.[10-12] In the one-mode system the peak frequency, characteristic of one end member of the solid solution, shifts continuously until it reaches the proper frequency of the other end member. The peak intensity is fairly constant. In the two-mode behavior both structures are present at the characteristic frequency of the end members: their intensity, and therefore their density of states, is proportional to the parent member concentration.

In the first hypothesis the LO-LA phonon frequency should shift from 39 cm^{-1} (Ref. 8) to at least 57 cm^{-1} as lighter cadmium atoms replace mercury in the crystal structure. The decay of A_{1g} in two or three LO-LA phonons must satisfy the energy conservation:

$$\Omega(A_{1g})=2\Omega(\text{LO-LA}) \text{ or } \Omega(A_{1g})=3\Omega(\text{LO-LA}) . \quad (3)$$

As the first condition for the two-phonon decay is achieved, theory predicts a sudden hybridization of the A_{1g} mode with the two-phonon states 2(LO-LA).[13] This coupling gives rise to a strong distortion of the A_{1g} line shape, which disappears when the resonance condition between the A_{1g} and the 2(LO-LA) phonon energy is lost. It should occur at higher cadmium concentrations when the frequency of the A_{1g} phonon becomes lower than 2Ω(LO-LA). Thereby the comparison between experiment and theoretical prediction rules out the one-mode behavior of these phonons.

In the two-mode hypothesis, the two LO-LA densities of states should be peaked at the characteristic frequencies of the HgI_2 and of the ideal CdI_2 with tetragonal structure. According to neutron scattering results,[8] the first one occurs at 39 cm^{-1} which corresponds to $\frac{1}{3}\Omega(A_{1g})$ and activates the three-phonon decay channel. Our results suggest that LO-LA phonons related to CdI_2 should be located at about 57 cm^{-1} so that energy is conserved in the two-phonon decay process. In such a way it is possible to explain the change of the efficiency of each decay channel. The quartic anharmonicity associated to the presence of mercury atoms decreases with cadmium concentration because the phonon density of states in which the A_{1g} decays becomes smaller. Instead the cubic anharmonicity increases for higher x values, being associated with the cadmium atoms.

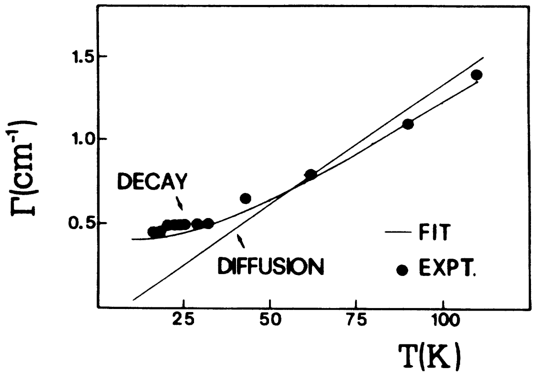

FIG. 4. A_{1g} linewidth for $x=0.38$ between 20 and 120 K. Solid lines represent the best fitting of the experimental data (points) when decay or diffusion processes are considered.

Finally it is possible to exclude a relevant contribution of the diffusion processes to the A_{1g} linewidth. These processes differ from the decay channels for the statistical weight.[14,15] This has the form n_1-n_2, where n_1 and n_2 are the Bose-Einstein factors of the phonons which are destroyed and created in the process. In Fig. 4 the solid line represents, for $x=0.38$, the theoretical contribution to Γ of a scattering event in which two phonons of 114 (A_{1g}) and 16 (LO or LA) cm^{-1} create an E_g^2 phonon of 130 cm^{-1}.[6] This condition is the best choice in order to fit the experimental data with diffusion processes. However, below 50 K, i.e., in the quantum-statistical limit, the agreement with experiment is inadequate. This is principally due to the fact that, at low temperature, diffusion processes give a small contribution to the Γ linewidth which is predicted to vanish at 0 K.

In conclusion we have studied a new mechanism which can influence the linewidth behavior of the Raman-active phonons in solid solutions: the change of the final density of states in the decay processes. This mechanism does not take its origin from the breakdown of the K-selection rules, but nevertheless it is peculiar to the alloying process in solid solutions. In this prospect interesting results should be expected from similar experiments in alloy systems that exhibit a fully or partially ordered cation sublattice.

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[1] D. J. Olego, P. M. Raccah, and J. P. Fourie, Phys. Rev. B **33**, 3819 (1986).

[2] J. M. Lopez Castillo and A. M. S. Tremblay, Phys. Rev. B **33**, 6599 (1986).

[3] B. Jusserand and J. Sapriel, Phys. Rev. B **24**, 7194 (1981).

[4] P. Parayanthal and F. H. Pollack, Phys. Rev. Lett. **52**, 1822 (1984).

[5] K. T. Tsen and H. Morkoç, Phys. Rev. B **37**, 7137 (1988); J. A. Kash, J. M. Hvam, and J. C. Tsang, in *International Conference on the Physics of Semiconductors, Warsaw, 1988*, edited by W. Zawadzki (Institut of Physics Polish Academy of Sciences, Warsaw, 1989).

[6] A. Anedda, G. Bongiovanni, and E. Fortin, Phys. Status Solidi B **146**, 757 (1988); A. Anedda and G. Bongiovanni, Phys. Rev. B **38**, 13 343 (1988).

[7] V. A. Haisler, V. M. Zaletin, and A. F. Kravchenko, Phys. Status Solidi B **125**, K103 (1984).

[8] B. Prevot, C. Schwab, and B. Dorner, Phys. Status Solidi B **88**, 327 (1978).

[9] T. Sakurai and T. Sato, Phys. Rev. B **4**, 583 (1971).

[10] A. S. Barker and A. J. Sievers, Rev. Mod. Phys. **47**, 52 (1975).

[11] F. I. Chang and S. S. Mitra, Adv. Phys. **20**, 359 (1971).

[12] P. N. Sen and W. M. Hartmann, Phys. Rev. B **9**, 367 (1974).

[13] J. Ruvalds and A. Zawadoski, Phys. Rev. B **2**, 1172 (1970).

[14] R. F. Wallis, I. P. Ipatova, and A. A. Maradudin, Fiz. Tverd. Tela (Leningrad) **8**, 1064 (1966) [Sov. Phys.—Solid State **8**, 850 (1966)].

[15] I. P. Ipatova, A. A. Maradudin, and R. F. Wallis, Phys. Rev. **155**, 882 (1967).