Theory of harmonic generation of ultrasound in $A15$ compounds

J. Noolandi
Bell Laboratories, Holmdel, New Jersey 07733
(Received 8 April 1974)

We explain the large second-harmonic generation of ultrasound observed in V_3Si by Testardi in terms of the interaction of the input shear wave with a dynamical strain induced by the low-temperature structural phase transition. We use the independent-chain model for the d electrons, and expand the free energy in powers of the total strain. The second-harmonic amplitude obtained by assuming a deviation from cubic symmetry arising from a homogeneous static strain is calculated to be too small to explain the experimental result.

In a recent experiment,[1] Testardi found a large rate of generation of second-harmonic ultrasound in V_3Si, using a shear wave propagated along the [110] direction, with polarization along $[1\bar{1}0]$, as the driving signal. This is a surprising result, because the symmetry of the crystal forbids the appearance of even-ordered harmonics for the shear wave propagated along the high-symmetry direction. In this paper we show that the effect is due to the anharmonic coupling of the shear wave to a dynamic strain, which distorts the shear wave and gives rise to second-harmonic generation. We show that the estimated amount of conversion of the fundamental wave to the second harmonic is in agreement with experiment, and that deviations from cubic symmetry due to a homogeneous static strain are too small to explain the effect.

We use the Weger-Labbé-Friedel model[2] of independent chains of d electrons, with the Fermi level near the Γ point of the reciprocal lattice. This model has been extended recently[3] to take into account the space-group symmetry of the crystal, and it gives a good description of the structural phase transition, as well as the temperature dependence of various quantities above and below the transition. The ultrasonic wave gives rise to a long-wavelength time-dependent strain in the crystal, and we use the deformation-potential theorem to calculate the energy shifts of the d electrons. To lowest order in the strains, the shift of the electron energies for the chains in the λ direction ($\lambda = x, y, z$) is

$$\delta E_\lambda = \sum_j \sigma_\lambda(j) d_j + \zeta_{\lambda\alpha\beta} s_{\alpha\beta} , \tag{1}$$

where

$$d_j = \sum_\kappa M_\kappa^{1/2} e_\alpha(\kappa | 0j) d_{\kappa\alpha} , \tag{2}$$

and $\sigma_\lambda(j)$, $\zeta_{\lambda\alpha\beta}$ are deformation-potential parameters,[3] $s_{\alpha\beta}$ denotes the strain, and $d_{\kappa\alpha}$ the displacement of sublattice κ, $e_\alpha(\kappa | 0j)$ is the polarization vector for a zero-wave-vector phonon, and the summation convention over repeated Greek indices is used. The d-electron thermodynamic potential per unit cell is

$$G_e = -k_B T N^{-1} \sum_{\lambda \vec{k}} \ln(1 + e^{(\mu - E_{\lambda\vec{k}})/k_B T}) , \tag{3}$$

where μ is the chemical potential and $E_{\lambda\vec{k}}$ is the d-electron energy in the strained lattice. The chemical potential is given by

$$N_d = -\frac{\partial G}{\partial \mu} , \tag{4}$$

where N_d is the number of d electrons per unit cell in the shallow band, and G is the sum of the electronic and lattice contributions to the thermodynamic potential. The harmonic part of the lattice potential energy given by[3]

$$\Phi = \frac{1}{2} \sum_j \Omega_j^2 d_j^2 + \tfrac{1}{2} Q_{\alpha\alpha'\beta\beta'} s_{\alpha\beta} s_{\alpha'\beta'} , \tag{5}$$

where $Q_{\alpha\alpha'\beta\beta'}$ and Ω_j are the high-temperature elastic constants and optical-phonon frequencies respectively, and we have neglected the bilinear coupling of the sublattice displacement to the strain for present purposes. For the total thermodynamic potential we take the sum of Eqs. (3) and (5). In this approximation the lattice anharmonicity enters only through the electronic contribution to the thermodynamic potential. Both the anharmonic terms in the lattice potential energy, and the higher-order terms in the deformation potential, Eq. (1), have been neglected. We use this approximation because it gives a good description of the structural phase transition, and the parameters in the thermodynamic potential have been accurately determined for this case.

We represent the applied shear strain by $[\epsilon, -\epsilon, 0]$, i.e., $s_{xx} = \epsilon$, $s_{yy} = -\epsilon$, $s_{zz} = 0$, and we expand the free energy,

$$F = \alpha\epsilon^2 + \beta\epsilon^3 + \gamma\epsilon^4 + \cdots . \tag{6}$$

For the wave vector in the [110] direction, the shears acting on the (110) plane in the $[1\bar{1}0]$ and $[\bar{1}10]$ directions give equivalent distortions of the

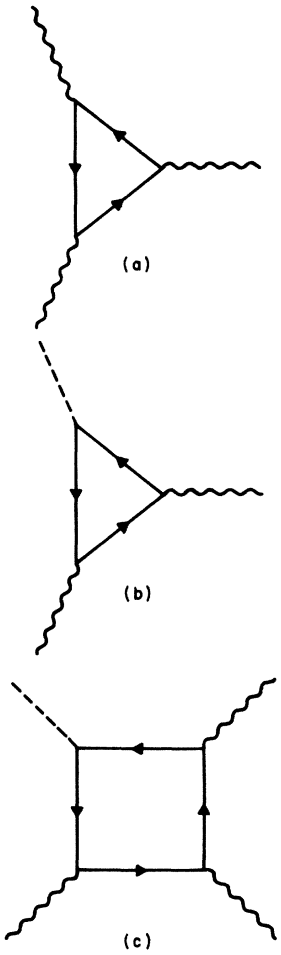

FIG. 1. Contributions to the free energy from interacting acoustic shear waves (~~~~), d electrons (————), and dynamic and static strains (– – – –).

crystal, and this leads to the vanishing of the odd-order terms in Eq. (6).[1] Hence, the contribution from the third-order electron-phonon scattering diagram, Fig. 1(a), vanishes for this case. However, it is possible to have a third-order contribution if one of the interacting waves is not a pure shear, as in Fig. 1(b). This can occur if the shear wave vector is not exactly in the [110] direction, as could be the case for actual experimental conditions,[4] and the crystal is very anharmonic. The strong anharmonicity couples the shear wave to the other vibrational modes of the crystal, and since the resultant can be distorted considerably from a pure shear wave, it can have a large second-harmonic component. Equivalently, since the symmetry argument given previously no longer holds, it is possible to have odd-order terms in the expansion given by Eq. (6).

The strong anharmonicity is responsible for the softening of the shear modulus and the cubic to tetragonal phase transition at low temperatures.[5] A tetragonal deformation can be written as a sum of shears on the (110) plane in the $[1\bar{1}0]$ direction, and on the (101) plane in the $[\bar{1}01]$ direction.[6] Since the solution of the nonlinear wave equation for strong anharmonicity and with the wave vector not along a high-symmetry direction is a formidable task, we make the assumption that the shear wave $[\epsilon, -\epsilon, 0]$ can interact with a dynamic strain of the form $[-\eta, 0, \eta]$. The total strain, $[\epsilon-\eta, -\epsilon, \eta]$, then has a component with the symmetry of the low-temperature tetragonal phase.

We estimate the energy flux of the second-harmonic wave at the receiving transducer to that of the fundamental by

$$\xi = (S_2/S_1)^2 , \tag{7}$$

where S_2, S_1 are the strain amplitudes, and we use ξ as a measure of the efficiency of conversion to the second harmonic. We write

$$S_2 = \simeq (\beta/\alpha)\,(x/\lambda)S_1^2 , \tag{8}$$

in analogy with the solution of the nonlinear wave equation for a longitudinal plane wave propagating along one of the high-symmetry directions in a cubic crystal.[7] Here α is the shear modulus and β the anharmonic coefficient corresponding to Fig. 1(b) in the expansion of the free energy in terms of ϵ and η. In writing Eq. (8) we have made use of the fact that $\beta \gg \alpha$. The path length is denoted by x, and λ is the wavelength of the fundamental. The anharmonic coefficient is obtained from Eqs. (1)–(5) and is given by

$$\beta = \left(\frac{\partial^3 F}{\partial \epsilon^2 \partial \eta}\right)_0 = -\left(\frac{\partial^2 \nu}{\partial \mu^2}\right) U^3 \left[\left(\frac{\Omega}{\omega}\right)^6 - \left(\frac{\Omega}{\omega}\right)^2 + 1\right], \tag{9}$$

where $U = \zeta_{1x} - \zeta_{1y}$ is the deformation potential, $\nu = N^{-1} \sum_{\vec{k}} n(\vec{k})$ is the occupation number per unit cell of one of the threefold degenerate d bands in the cubic phase, and $\omega^2 = \Omega^2 - 6\sigma^2 (\partial \nu/\partial \mu)$ is the temperature-dependent Γ_{12} optical-phonon frequency. In deriving Eq. (9) we have calculated the derivatives of the sublattice displacements making use of the equilibrium conditions $\partial F/\partial d_j = 0$, which define the sublattice displacements as implicit functions of ϵ and η. We have also used the fact that only the Γ_{12} optical mode is coupled to the shear wave.[8]

We calculate the second-harmonic strain amplitude for Nb_3Sn, since at present the parameters for this crystal are known more accurately than for V_3Si. There should not be any significant difference in the second-harmonic generation for the two crystals, since both have similar temperature-dependent properties, and transform to a tetragonal state at low temperatures. Using Eqs. (7)–(9) and the constant-density-of-states model for Nb_3Sn,[3,9] with $T = 1.5 T_m \simeq 70$ K, we get $\xi \simeq 0.05$, where we

have used $x = 1$ cm for the path length and $\lambda = 0.025$ cm for a 5-MHz driving signal in Nb_3Sn at $T = 70$ K. The strain amplitude of the fundamental wave is between 10^{-6} and 10^{-5},[1] and we have used $S_1 = 5 \times 10^{-6}$. Including the attenuation of the fundamental does not significantly alter the estimate of the conversion efficiency because the assumed temperature is well above T_m, and the path length is relatively short. Testardi has estimated that the maximum energy ratio of the second harmonic to the fundamental at the receiving transducer was about 20% for the highest drive levels. The calculated value of 5% is in satisfactory agreement, considering the uncertainties in the experiment and the theoretical interpretation. The present theory assumes that the slope of the received signal amplitude to the drive level is 2, and we are unable to explain why the experimental result is greater than this value. It remains to be seen whether a more complete perturbation treatment of the free energy and the nonlinear wave equation can explain this deviation, as well as the linear dependence of the received signal amplitude on the drive level at the highest drive levels.

If the crystal is assumed to deviate from cubic symmetry because of a homogeneous static strain of order 10^{-4}, then the fourth-order term in the free energy corresponding to Fig. 1(c) contributes to the second-harmonic generation. For this case the anharmonic coefficient γ in Eq. (6) can be calculated as before by differentiating the free energy with respect to the strains, with $\partial F/\partial d_j = 0$, and the corresponding fourth-order contribution, Fig. 1(c), is found to be several orders of magnitude smaller than the third-order contribution, Fig. 1(b), with a dynamic strain, and hence can be neglected. The third-order diagram gives no contribution to the second-harmonic amplitude for the case of a homogeneous static strain.

It would be interesting to measure the amount of second-harmonic generation in nontransforming crystals of V_3Si and Nb_3Sn, and in the other nontransforming $A15$ compounds, since the present theory predicts that the second-harmonic amplitude would be less in these crystals.

It is a pleasure to acknowledge many stimulating discussions with L. R. Testardi and several helpful discussions with R. N. Thurston.

[1]L. R. Testardi, Phys. Rev. Lett. 31, 37 (1973).
[2]M. Weger, Rev. Mod. Phys. 36, 175 (1964); J. Labbé and J. Friedel, J. Phys. (Paris) 27, 153 (1966); 27, 303 (1966).
[3]J. Noolandi and L. J. Sham, Phys. Rev. B 8, 2468 (1973).
[4]The wave vector may deviate from the [110] direction by a few degrees. Another source of symmetry reduction is the possible occurrence of small amounts of a second phase, V_5Si_3, in the crystal of V_3Si [L. R. Testardi (private communication)]. However, we would like to emphasize that the large second-harmonic amplitude observed experimentally is not due directly to these effects, but arises because a small source of symmetry reduction allows the strong anharmonicity to couple the shear wave to the tetragonal fluctuations.
[5]For a review of experimental and theoretical work on the $A15$ compounds see L. R. Testardi, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. 10, p. 193.
[6]B. W. Batterman and C. S. Barrett, Phys. Rev. 145, 296 (1966).
[7]M. A. Breazeale and J. Ford, J. Appl. Phys. 36, 3486 (1965).
[8]L. J. Sham, Phys. Rev. Lett. 27, 1725 (1971).
[9]R. W. Cohen, G. D. Cody, and J. J. Halloran, Phys. Rev. Lett. 19, 840 (1967).