pared to experimental values. More pertinent in connection with photoemission are the placements of the $4f$ states obtained by the multielectron method taking into account relaxation effects when one electron is removed. The multielectron predictions for the $4f$ shells are approximately[13] 4.1 and 5.1 eV for Pr and Nd, respectively. In addition to the valence-band structures which remain stationary, the XPS spectra show $4f$ peaks at 3.4 eV for Pr and 4.8 eV for Nd, in fairly good agreement with the computed values. The spectrum of Ce does not show clearly the separation between d and f states. The flat shape of the broad peak indicates however that two unresolved structures are present. In connection with this XPS spectrum, it is useful to consider the energy distribution curve of photoelectrons excited by uv light.[14] The curve recorded for a clean Ce surface shows the typical feature of an s-d band, while no evidence of a $4f$ level can be observed. It seems reasonable to assume that our spectrum is formed by a valence band rather similar to that of La and by a $4f$ peak at higher binding energies. An approximate deconvolution yields an energy of 1.8 eV for the $4f$ level, in good agreement with the value of 2.0 eV predicted by the multielectron calculation. Our interpretation of the four spectra is strengthened by the observation of the relative intensity increase from Ce to Nd of the $4f$ signal compared to the valence-band signal. Unfortunately the separation of the two structures and the subtraction of the background are too arbitrary for a precise intensity determination. The spectra have been tentatively normalized to the intensity of the $5p$ core levels. The valence-band intensities are then contained in a range of $\pm 20\%$ around a mean value while the $4f$ intensities are nearly proportional to the expected number of these electrons, i.e. 1 to 3 from Ce to Nd. It is clear from these results that the probability per electron of excitation by soft x rays is of the same order of magnitude for d and f symmetry. Thus, the spectra presented in this study can be considered as rather reliable pictures of the outer levels of light rare-earth metals.

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[1]P. O. Hedén, H. Löfgren, and S. B. M. Hagström, Phys. Rev. Lett. 26, 432 (1971).
[2]S. B. M. Hagström, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 515.
[3]P. O. Hedén, H. Löfgren, and S. B. M. Hagström, Phys. Status Solidi (b) 49, 721 (1972).
[4]G. L. Lapeyre, Phys. Rev. 179, 623 (1969).
[5]D. E. Eastman, Solid State Commun. 7, 1697 (1969).
[6]G. Brodén, Phys. Kondens. Mater. 15, 171 (1972).
[7]G. Brodén, S. B. M. Hagström, and C. Norris, Phys. Kondens. Mater. 15, 327 (1973).
[8]See Ref. 1, Fig. 3. As far as we know, the Pr spectrum has never been published.
[9]We have measured the whole series from La to Lu. A complete report will be published elsewhere.
[10]Y. Baer, P. F. Hedén, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, Phys. Scr. 1, 55 (1970).
[11]S. C. Keeton and T. L. Loucks, Phys. Rev. 168, 672 (1968).
[12]J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B 6, 1913 (1972).
[13]The numerical values have been estimated from Fig. 7 of Ref. 12.
[14]C. R. Helms and W. E. Spicer, Appl. Phys. Lett. 21, 237 (1972).

Harmonic-Phonon Generation by Shear Waves in V_3Si

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The generation of second-harmonic ultrasound (5 to 10 MHz) with an estimated conversion efficiency $\gtrsim 20\%$ has been observed for the soft shear mode in V_3Si below 77°K. The harmonic generation is a manifestation of the unusually large shear anharmonicity for this unstable compound; however, static symmetry arguments forbid the generation of an even-ordered harmonic for a high-symmetry shear wave in a cubic crystal. Several possible sources of symmetry reduction are discussed.

The A-15 structure compounds have provided the first and the most detailed examples of the interrelation of structural instability and high-temperature superconductivity.[1-4] In addition to the soft modes and structural transformations exhibited by these compounds, a complicating but

often crucial property of these materials relevant to their anomalous behavior is an unusual degree of anharmonicity.[4-7] This Letter reports a striking manifestation of this anharmonicity —the generation of second-harmonic sound with exceptional efficiency by the "soft" shear mode in V_3Si at temperatures well above that at which the structural transition occurs. A significant feature of these results is that symmetry arguments would forbid the occurrence of even-ordered harmonics in this case. Several explanations are offered, one of which indicates that because of anharmonicity the symmetry of soft-mode unstable materials may slightly deviate from the ideal state assumed to exist at high temperatures.

Pulsed shear-mode sound waves at 5 MHz with propagation direction $\vec{q} \| [110]$ and particle motion $\vec{p} \| [1\bar{1}0]$ were launched with a 5-MHz Y-cut quartz transducer at one end of a single crystal of V_3Si. The sample length ($\| \vec{q}$) was 12 mm, and the transverse dimensions were ~7–10 mm. A 10-MHz Y-cut quartz transducer with the same polarization at the opposite end of the sample acted as a detector for the sound waves after a single transit of the sample. The arrangement is shown in Fig. 1. Observations of the harmonic generation were made in several experiments using different transducers, bonds, and impedance-matching networks. Temperatures were obtained from a simultaneous measurement of the sound velocity which provides a convenient measurement of bulk-sample temperature during the experiment.[2] All observations were made at temperatures well above that of the structural transformation (~21° K). For $T < 21$°K sound propagation could not be detected.

At room temperature, only a weak 5-MHz signal was observed from the 10-MHz receiving transducer, indicating that harmonic generation is neither detectable at room temperature nor due to nonlinear response of the electronic systems. At 120°K, where again only the fundamental was seen, this signal was linearly dependent on drive level between 30 and 400 V (rms) on the driving transducer. At the lower temperatures, however, the strong second-harmonic generation shown in Fig. 2 was observed. Note that the received signal (Fig. 2, lower) is almost entirely the second harmonic of the driving signal (Fig. 2, upper). The ratio of fundamental to second harmonic depended on both the driving amplitude and the temperature. I consider first the former.

Simultaneous measurements of the driving and received signals showed the nonlinear dependence given in Fig. 3. The 10-MHz signal was observed to increase approximately as the cube of the drive level at low drive levels, and linearly with drive level at the higher levels.

An estimate of the acoustic strains generated by the driving transducer from the applied voltage was made using the method outlined by Alers and Fleury.[8] Ignoring bond effects and attenuation, the calculated strain at the highest drive

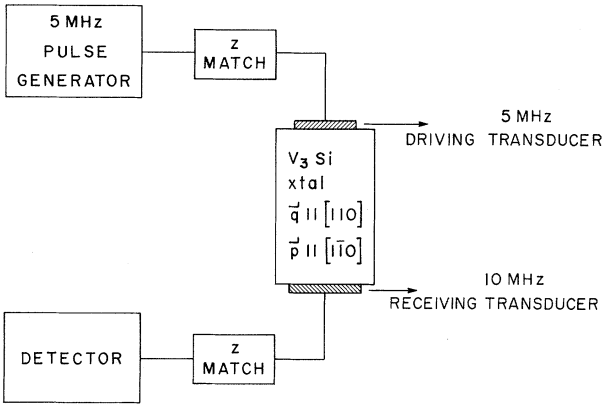

FIG. 1. Experimental arrangement for harmonic-generation detection. The driving signal was monitored between the pulse generator and the impedance (Z) matching network. The signal on the driving transducer was obtained from the monitored signal by calculation from the Z match network and by independent measurement.

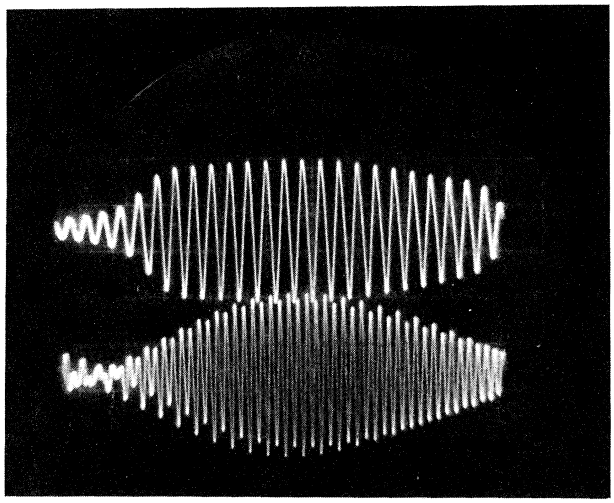

FIG. 2. Oscilloscope photograph of the driving signal applied to the 5-MHz transducer (upper) and the amplified 10-MHz receiving-transducer signal (lower). The delay due to the sound transit time along the crystal is not shown. $T \approx 40$°K.

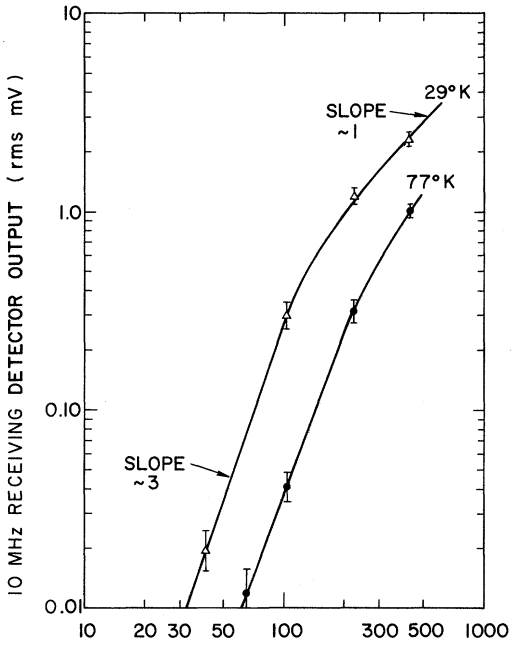

FIG. 3. 10-MHz received signal amplitude as a function of the 5-MHz drive level showing nonlinearity in the harmonic generation at 29 and 77°K. As discussed in the text the relative amplitudes at the two temperatures may not reliably be compared.

level used was ~ 10^{-5}.

The dependence of the absolute second-harmonic amplitude on temperature at fixed drive level could not be determined with great accuracy since the insertion loss of both sample-transducer bonds, which depends on temperature, could not be easily established. Indeed, in several temperature cycles (80–4–80°K) the absolute amplitudes varied by factors of 2 to 4—a change not unusual in normal ultrasonic experiments with temperature cycling. It was generally true, however, that for fixed drive level the received second-harmonic signal increased on cooling while the received fundamental, as established from previous attenuation studies,[2,4] decreased. In addition, the linear dependence of the second harmonic on drive level is reached at lower drive levels with decreasing temperature.

The harmonic-generation observations discussed above might be influenced by phase-matching conditions for the frequency used. For our experiment phase cancelation of fundamental and harmonic would occur if the velocity of the 10-MHz waves were ~0.4% to 0.8% different from that of the fundamental. Because of the strong attenuation at low temperatures it is not possible to achieve much greater accuracy than 0.4% in velocity measurements as a function of frequency, and one must allow the possibility of some phase-matching problems in these observations.

Finally, the actual efficiency of conversion can be estimated, though only roughly, from the following observations. At 100°K, where strong harmonic generation was not observed, the ratio of 5-MHz signal amplitude at the receiving detector to the echoes received at the driving transducer was $\frac{1}{60}$. Assuming this ratio to be temperature independent, and from the observation that at lower temperatures and high drive levels no fundamental was seen to within ± 4% in amplitude, leads to the estimate that the (energy) ratio of 10 to 5 MHz at the receiving transducer was >20%. Corrections (compensatory) for the attenuation of the 5- and 10-MHz signals along the sample length are difficult to make but should not alter the above result by more than a factor of 2.

The occurrence of such efficient harmonic generation by sound waves of such small strain amplitude indicates the large degree of anharmonicity for these unstable compounds. This anharmonicity is a complicating factor which is crucial to understanding some of the anomalous behavior of these compounds.

The occurrence of an even-ordered harmonic generation[9] is, however, unexpected in view of simple symmetry arguments. If we expand the (free or internal) energy of a solid in terms of the strain ϵ,

$$U = \alpha\epsilon^2 + \beta\epsilon^3 + \cdots, \quad (1)$$

it is readily seen that the generation of the second harmonic is related to the strength of the anharmonic coefficient β (α is twice the elastic modulus at zero strain). However, for a high-symmetry shear strain all of the coefficients odd ordered in ϵ must vanish since positive- and negative-type shear strains lead to identical structures; therefore, the generation of even-ordered harmonics should not occur. Two possibilities can be considered then to account for the occurrence of second-harmonic generation in this experiment. The first is that there was sufficient misorientation of mode propagation[10] for Eq. (1) not to apply. One test of this would be the observation of extraneous modes (which in V_3Si are not strongly attenuated at any temperature) which would result from such misorientation. At 4.2°K, however, no echoes of any type were observed, leading to the estimate that at temperatures where

harmonic generation was seen extraneous modes were at least 30 dB below that of the soft shear mode. This result, as well as x-ray orientation studies, precludes large misorientation effects. In estimating small misorientation effects several other sources of symmetry reduction should now be considered.

If, in Eq. (1), ϵ is interpreted as a volume strain, then, at finite temperature where thermal strains lead to a finite ϵ, the asymmetrical potential described by Eq. (1) will cause the system, on the average, to be in a state of finite strain ϵ. From a simple calculation of the difference in time spent in the soft (negative ϵ) and stiff (positive ϵ) sides of the potential one finds that at high temperatures an average strain $\langle\epsilon\rangle \sim -kT\beta/4\alpha^2$, which is just the classical thermal expansion.[11] Similar arguments will lead to a tetragonal expansion provided that a (minor) source of symmetry reduction exists. That such sources always exist is evidenced by the fact that in the transformed state (below 21°K) the c axis is almost always aligned with the same cubic-state a axis. Thus, because of the large anharmonic coefficient β, those factors which "align" the tetragonal axes relative to the cubic axes will cause the symmetry in the high-temperature phase to deviate from that assumed for the ideal case. The source of the symmetry reduction may be small strains either inadvertently applied in the experiment or intrinsic to the crystal, its shape or boundaries. Such strains, certainly if intrinsic, must be small since both x-ray[1] and neutron[12] studies have shown these single crystals to be of high quality. Noncubic behavior of V_3Si has been indicated in previously published thermal-expansion studies of Fawcett.[13] Carcia, Barsch, and Testardi[14] have also obtained evidence of noncubic behavior in V_3Si under pressure. These results suggest that on a scale of 10^{-4}–10^{-6} the symmetry of V_3Si is noncubic above 21°K. These strains are comparable to those impressed by the sound wave and thus would make second-harmonic generation possible for crystals of unusually large anharmonicity.[15]

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[1]B. W. Batterman and C. S. Barrett, Phys. Rev. Lett. 13, 390 (1964).

[2]L. R. Testardi, W. A. Reed, T. B. Bateman, and V. G. Chirba, Phys. Rev. Lett. 15, 250 (1965).

[3]K. R. Keller and J. J. Hanak, Phys. Lett. 21, 263 (1966).

[4]For a review and more complete list of references see L. R. Testardi, in "Physical Acoustics," edited by W. P. Mason and R. N. Thurston (Academic, New York, to be published), Vol. X.

[5]Evidence for large anharmonic forces in Nb_3Sn from Mössbauer studies have been obtained by J. S. Shier and R. D. Taylor, Solid State Commun. 5, 147 (1967), and Phys. Rev. 174, 346 (1968). No direct measurements of the anharmonicity in Nb_3Sn have been reported.

[6]J. R. Patel and B. W. Batterman, Phys. Rev. 148, 662 (1966).

[7]L. R. Testardi, Phys. Rev. B 5, 4342 (1972).

[8]G. A. Alers and P. A. Fleury, J. Acoust. Soc. Amer. 36, 1297 (1964).

[9]A search for third-harmonic generation (10 to 30 MHz) was unsuccessful. In this case the receiving transducer responds well to the driving signal, and this fact, together with the increased attenuation at the higher frequencies, makes the detection of a weak harmonic generation (< 1%) difficult.

[10]Misorientation of the polarization direction in the (110) plane would not lead to harmonic generation.

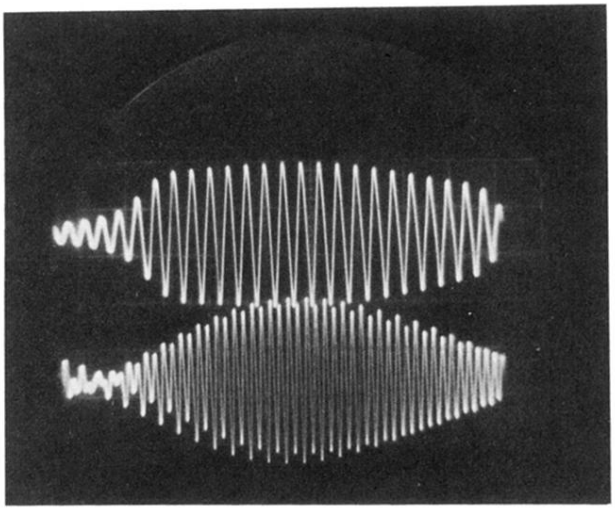
[11]For a derivation from statistical mechanics see C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1956), 2nd ed., p. 152.

[12]G. Shirane, J. D. Axe, and R. J. Birgeneau, Solid State Commun. 9, 397 (1971).

[13]E. Fawcett, Phys. Rev. Lett. 26, 829 (1971).

[14]P. F. Carcia, G. R. Barsch, and L. R. Testardi, Phys. Rev. Lett. 27, 944 (1971).

[15]As an alternative explanation for the second harmonic generation, W. P. Mason (private communication) has suggested that the stress-strain "loop" for V_3Si may be "figure 8" or "pinched" shaped. For the case of ferroelectrics (where displacement and electric field are the corresponding parameters) a similar behavior has been observed and explained as a field-induced transition to a ferroelectric phase. The analogy in our case—a stress-induced structural transformation carried by the sound wave—appears unlikely for the stress of our sound wave. J. R. Patel and B. W. Batterman [J. Appl. Phys. 37, 3447 (1966)] have shown that for uniaxial stresses (these are nearly pure shear type in V_3Si at low temperature) which exceeded those in our sound wave by ~2 orders of magnitude the structural transition temperature was changed by < 0.1°K. This effect is too small to explain our observations at 77°K. Other sources of irregular stress-strain loops may, however, play a role.



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