ergy, as observed in Fig. 1.

From our tunneling experiment on a clean tantalum junction, we believe that the existing theory of superconductivity based on the electron-phonon interaction explains the behavior of one transition metal. Neither the small zero-bias conductance peak in the normal state, nor the relatively large change in background conductance with bias, seems to affect the superconducting density of states which is obtained by normalizing two measured tunneling conductances. Melting of small samples in ultrahigh vacuum is capable of producing good quality junctions and can hopefully be applied to other transition metals.

The author wishes to thank J. M. Rowell, W. L. McMillan, and R. C. Dynes for many helpful suggestions.

[1]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[2]J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964), and references therein.

[3]See, for example, *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. I, and references therein.

[4]W. L. McMillan and J. M. Rowell, Phys. Rev. Letters 14, 108 (1965).

[5]See, for example, B. T. Matthias, in *Superconductivity*, edited by P. R. Wallace (Gordon and Breach, New York, 1969), Vol. I, p. 225; or B. T. Matthias, C. W. Chu, E. Corenzwit, and D. Wohlleben, Proc. Natl. Acad. Sci. U. S. 64, 459 (1969).

[6]J. J. Engelhardt, G. W. Webb, and B. T. Matthias, Science 155, 191 (1967).

[7]C. G. Kuper, M. A. Jensen, and D. C. Hamilton, Phys. Rev. 134, A15 (1964).

[8]R. D. Fowler, J. D. G. Lindsay, R. W. White, H. H. Hill, and B. T. Matthias, Phys. Rev. Letters 19, 892 (1967).

[9]B. T. Matthias, T. H. Geballe, K. Andres, E. Corenzwit, G. W. Hull, and J. P. Maita, Science 159, 530 (1968).

[10]A. F. G. Wyatt, Phys. Rev. Letters 13, 160 (1964).

[11]J. S. Rogers and S. M. Khanna, Phys. Rev. Letters 20, 1284 (1968).

[12]I. Dietrich, Z. Naturforsch. 17a, 94 (1962).

[13]P. Townsend and J. Sutton, Phys. Rev. 128, 591 (1962).

[14]L. Y. L. Shen and J. M. Rowell, Phys. Rev. 165, 566 (1968).

[15]C. A. Neugebauer and R. A. Ekvall, J. Appl. Phys. 35, 547 (1964).

[16]H. J. Levinstein and J. E. Kunzler, Phys. Letters 20, 581 (1966).

[17]See Ref. 3, p. 580.

[18]L. F. Mattheiss, Phys. Rev. 1, 373 (1970).

[19]See Ref. 3, pp. 588-593.

[20]L. Y. L. Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Letters 14, 1025 (1965).

[21]G. M. Éliashberg, Zh. Eksperim i Teor. Fiz. 38, 966 (1960) [Soviet Phys. JETP 11, 696 (1960)].

[22]P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[23]W. L. McMillan, Phys. Rev. 167, 331 (1968).

[24]A. D. B. Woods, Phys. Rev. 136, A781 (1964).

[25]R. C. Dynes, J. P. Carbotte, and E. J. Woll, Jr., Solid State Commun. 6, 101 (1968).

[26]J. M. Rowell, W. L. McMillan, and W. L. Feldmann, Phys. Rev. 178, 897 (1969).

[27]R. C. Dynes and J. M. Rowell, Phys. Rev. 187, 821 (1969).

[28]A. P. Roy and B. N. Brockhouse, to be published.

[29]W. Kohn, Phys. Rev. Letters 2, 393 (1959).

[30]J. Peretti, I. Pelah, and W. Kley, Phys. Letters 3, 105 (1962).

[31]Y. Nakagawa and A. D. B. Woods, Phys. Rev. Letters 11, 271 (1963).

HYBRID PHONONS AND ANHARMONIC INTERACTIONS IN $AlPO_4$

J. F. Scott
Bell Telephone Laboratories, Holmdel, New Jersey 07733
(Received 3 February 1970)

We have observed, by means of Raman studies at elevated temperatures, strong anharmonic interactions between one-phonon states and between one- and two-phonon states in aluminum phosphate. These result in striking destructive interference of scattering amplitudes and in the formation of coupled modes. Hybridization of one- and two-phonon states is compared with that observed in quartz.

Four kinds of coupled-mode interaction involving only phonons have previously been demonstrated by Raman studies on crystals. The first and simplest is illustrated in the spectra of $SrTiO_3$.[1] Two phonons of the same symmetry are near in frequency; one is strongly electric-field dependent and is swept through the energy of the second by application of an external field. Each phonon has a linewidth which is smaller than the distance of closest approach, i.e., the

interaction energy, and no line-shape anomalies occur, only an intensity transfer and anticrossing or level-repulsion characteristic of coupled harmonic oscillators. The second case has been illustrated in α-quartz.[2] A temperature-dependent one-phonon state interacts with a two-phonon state as it is swept through the latter. The interaction is again well approximated by coupled "harmonic" oscillators—only because the interaction between the one- and two-phonon states is a little larger than their linewidths. Recently Ruvalds and Zawadowski have made many-body calculations which justify the phenomenological coupled-mode description in quartz.[3] The third case is that illustrated by Rousseau and Porto[4] in $BaTiO_3$: A sharp one-phonon state interacts with a background continuum. In this case, unlike those in $SrTiO_3$ and quartz, there are striking line-shape anomalies and strong interference effects. The data are accurately described by Fano's theory[5] of Auger-like processes, which details interference effects associated with coupled discrete and continuum states. While Rousseau and Porto described their observed interaction as between one- and two-phonon states, more detailed study of $BaTiO_3$ indicates[6] that it actually illustrates only one-phonon interactions. Although the $BaTiO_3$ "continuum" is broad and rather featureless, it is apparently due to a heavily damped one-phonon excitation. The fourth case of coupled modes is the two-phonon bound state in diamond analyzed by Cohen and Ruvalds.[3]

In the present Raman study of $AlPO_4$ we have been able to probe two of the kinds of anharmonic interaction discussed above: the one-phonon state interactions characteristic of $BaTiO_3$, and the one- and two-phonon state interactions observed in quartz. In comparison with the work of Rousseau and Porto, who were able to vary the interference in $BaTiO_3$ by selecting different polarization phonons propagating along different axes but were not able to change the phonon frequencies, the present study includes striking temperature effects—the broad feature is "tuned" continuously through the sharp mode by varying temperature. Combined with earlier work on quartz, the new $AlPO_4$ data show how powerful soft optic modes are as a probe of anharmonic interactions.

The temperature dependence of the soft mode in $AlPO_4$ triggering the α-β phase transition is shown in Fig. 1. The linewidth over the same

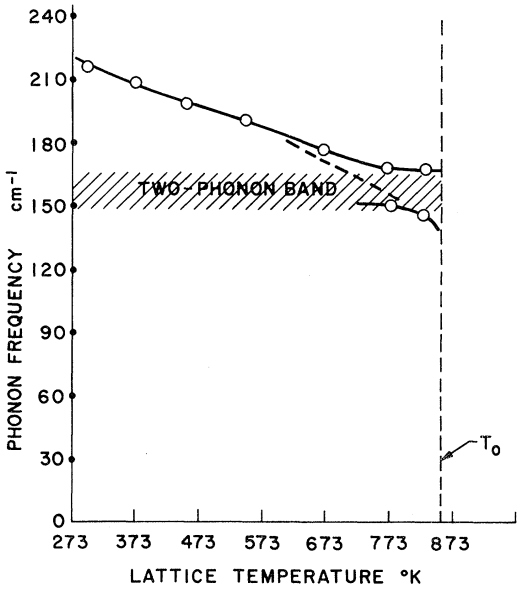

FIG. 1. Frequency versus temperature for the soft mode in $AlPO_4$ triggering the α-β phase transition.

temperature region (300-840°K) varies linearly from 20 ± 5 cm^{-1} at 300°K (full width at half-height) to 80 ± 10 cm^{-1} at ~840°K. At temperatures below 300°K the spectrum is strikingly similar to that of isomorphic α-quartz. A feature at about 200 cm^{-1} of A_1 symmetry broadens and decreases in frequency with increasing temperature. It is very nearly Lorentzian in shape at low temperatures, and below 400°K no interaction between the soft mode and the A_1 mode at 158 cm^{-1} is apparent. (While $AlPO_4$ is isomorphic to α-quartz and has the same A_1 soft mode at ~200 cm^{-1}, it has additional A_1- and E-symmetry modes at lower frequencies; this is because the unit cell is twice as long as that of quartz in the c direction, owing to the substitution of Al and P ions in alternate silicon sites. The assignment of these new modes can be made from Elcombe's [001] inelastic neutron scattering data on quartz,[7] and will be detailed in a later publication). Above 400°K a striking anharmonic interaction between the soft mode and the A_1 phonon at 158 cm^{-1} occurs, which is shown in Fig. 2. This interaction is accurately described via a Green's function treatment in the accompanying paper by Zawadowski and Ruvalds (ZR).[8] The data shown can also be described by Fano's formalism.

In Fano's notation, as used by Rousseau and Porto,[4,5] the amplitude for scattering into a coupled discrete-plus-continuum state is given

by

$$\langle\Phi(\text{hybrid})|\alpha_{ij}|\Phi(0)\rangle=[W\langle\Phi(\text{disc})|\alpha_{ij}(\text{disc})|\Phi(0)\rangle+(E-E_0-F)\langle\Phi(\text{cont})|\alpha_{ij}(\text{cont})|\Phi(0)\rangle]\times[(E-E_0-F)^2+\pi^2|W|^4]^{-1/2}. \quad (1)$$

Here $\Phi(0)$ is the no-phonon ground state; $\Phi(\text{disc})$ and $\Phi(\text{cont})$, the discrete and continuum states with energies E_0 and E; F, the shift in resonance energy due to the interaction (equivalent to Δ in the usual Green's function notation); α_{ij}, the polarizability tensor element for the state designated in parentheses; and $W=\langle\Phi(\text{disc})|H_{\text{anh}}\times|\Phi(\text{cont})\rangle$. The change in sign of the numerator in Eq. (1) at $E=E_0+F$ causes a characteristic antiresonance lineshape.

In Fano's theory a one-phonon state is viewed as interacting with a continuum. The physical origin of the Raman interference is cancellation of scattering amplitudes to the one-phonon state $\langle\Phi_1|$ from the ground state $|\Phi(0)\rangle$:

$$\langle\Phi_1|\alpha^{(1)}|\Phi(0)\rangle$$

and

$$\langle\Phi_1|W|\Phi(\text{cont})\rangle\langle\Phi(\text{cont})|\alpha|\Phi(0)\rangle.$$

It is important that $\langle\Phi(\text{cont})|\alpha|\Phi(0)\rangle$ is only vaguely defined. Rousseau and Porto and Ruvalds and Zawadowski all equate $\Phi(\text{cont})$ with backgrounds associated with two acoustic phonons, but evaluate $\langle\Phi(\text{cont})|\alpha|\Phi(0)\rangle$ in completely different ways. Rousseau and Porto assume

$$\langle\Phi(\text{cont})|\alpha|\Phi(0)\rangle=\langle\Phi(\text{cont})|\alpha^{(2)}|\Phi(0)\rangle, \quad (2)$$

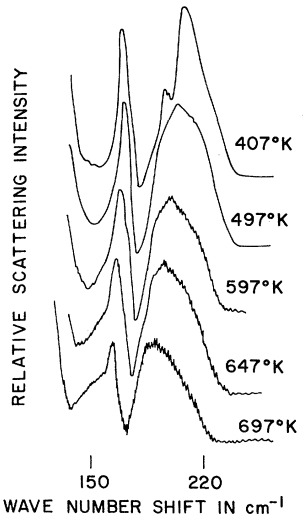

FIG. 2. Temperature dependence of the Fano-type resonance at ~160 cm^{-1} in $AlPO_4$. The middle bump in the uppermost trace is an E mode of no present interest.

i.e., a direct second-order Raman transition. Zawadowski and Ruvalds assume

$$\langle\Phi(\text{cont})|\alpha|\Phi(0)\rangle=\langle\Phi(\text{cont})|H_3|\Phi_2\rangle\times\langle\Phi_2|\alpha^{(1)}|\Phi(0)\rangle, \quad (3)$$

i.e., first-order Raman transition to a one-phonon state Φ_2 followed by three-phonon interaction due to cubic anharmonicity (see Fig. 1 of ZR). Fano's theory is sufficiently general to encompass both contributions to $\langle\Phi(\text{cont})|\alpha|\Phi(0)\rangle$; however, the experimental data on both $BaTiO_3$[6] and $AlPO_4$ support the assumption of Ruvalds and Zawadowski that only first-order processes occur. While the $\Phi(\text{cont})$ states summed over in the accompanying Green's function calculation (ZR) are implicity specified as two-phonon states (since only three-phonon interactions are included), we show in the following section that those in $AlPO_4$ consist primarily of $2TA^K$, two transverse acoustic phonons at critical point K.

In concluding this phase of the discussion, we wish to emphasize the difference between one-phonon couplings in $SrTiO_3$ and $AlPO_4$: In $SrTiO_3$ the optic phonons are directly coupled (via an electric field); in $AlPO_4$ (and $BaTiO_3$) they are indirectly coupled via the anharmonic terms linkine each to the two-acoustic-phonon background.

We now turn to the second anharmonic coupling in Al PO_4. The interaction between one- and two-phonon states like that in quartz does not appear in $AlPO_4$ until very near the phase transition at ~852°K.[9] As the soft mode moves toward 164 cm^{-1} a small satellite at 147 cm^{-1} grows in intensity and moves to lower energies, while the main peak is pinned at about 164 cm^{-1}. This is identical to the observation in quartz; refer to Ref. 2 for details. Even the frequency (147-164 cm^{-1}) of the inferred two-phonon state is the same (see Fig. 1). The data are shown in Fig. 3 and are somewhat less distinct than in quartz on account of the 158-cm^{-1} mode interaction and the presence of another strong line at lower frequencies.

Some information exists concerning the location in the Brillouin zone of the 73-cm^{-1} acoustic phonons which cause the 147-cm^{-1} peak. Miss Elcombe's inelastic neutron studies[7] on quartz show that the zone-edge transverse acoustic

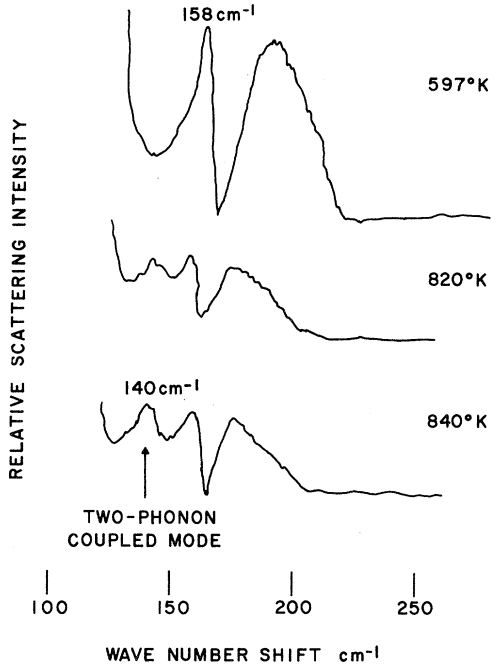

FIG. 3. Temperature dependence of the one- and two-phonon coupled mode resonance in $AlPO_4$. The strong line at ~ 115 cm^{-1} is an E (TO + LO) phonon.

mode at $q = (\pi/c)(0, 0, 1)$ is at ~50 cm^{-1}. Hence Professor Leadbetter's (70 ± 5)-cm^{-1} peak in the one-phonon density of states inferred from inelastic neutron scattering[10] in polycrystalline quartz must originate elsewhere in the zone. From Miss Elcombe's model calculation[7] we infer that the most likely location of the contributing acoustic phonons in both quartz and $AlPO_4$ is at critical point K, which is $q = (2\pi/a)(\frac{2}{3}, 0, 0)$. We tentatively assign the two-phonon state as $2TA^K$ and encourage the inealstic neutron study of the acoustic branches in quartz at K in order to provide verification.

As in quartz, it is satisfactory to treat the interaction as a cubic anharmonic coupling of one optical phonon at $q = 0$ and two acoustic phonons at $q = K$ and $-K$. Both the quartz and $AlPO_4$ data can be described by the coupled-mode equation

$$\omega_\pm = \tfrac{1}{2}(\omega_1 + \omega_2) \pm \tfrac{1}{2}[(\omega_1 - \omega_2)^2 + 4|W|^2]^{1/2}, \qquad (4)$$

where ω_2 is the temperature-independent two acoustic-phonon state at ~145 cm^{-1} and ω_1 is the temperature-dependent soft optic phonon; W is the off-diagonal matrix element in the anharmonic Hamiltonian connecting the two states. In quartz the data show that W^2 is proportional to the linewidth of the soft mode, or since that linewidth varies linearly with temperature, $W^2 = AT$, with $A \approx 1.6$ cm^{-2} (°K)$^{-1}$. In $AlPO_4$ the existing data are too scanty to determine the form of W, although some theoretical justification for $W^2 = AT$ dependence has been cited by Shapiro,[2] and we shall assume that form is generally valid. Since the distance of closest approach (equal to $\sim 2W$) of the one- and two-phonon maxima in the spectra are the same in quartz and in $AlPO_4$ and occur at about the same temperature, we infer a value of $A \approx 1.6$ in $AlPO_4$ also.

We note that, as shown in Fig. 1, the soft mode will not intersect $\omega = 0$ at $T_0 = 852$°K. This shows that the phase transition is not exactly second order, in analog with α-quartz.

The excellent $AlPO_4$ samples were grown by Dr. R. Lang at McMaster University and provided to the author through the courtesy of Professor Crespin Calvo. We thank L. E. Cheesman for his usual excellent technical assistance also, and J. M. Worlock for helpful discussions.

[1]J. M. Worlock, J. F. Scott, and P. A. Fleury, in *Light Scattering Spectra of Solids*, edited by G. Wright (Springer, New York, 1969), p. 689.

[2]J. F. Scott, Phys. Rev. Letters 21, 907 (1968); S. M. Shapiro, thesis, Johns Hopkins University, 1969 (unpublished).

[3]J. Ruvalds and A. Zawadowski, Phys. Rev. (to be published). This paper contains detailed line-shape calculations which agree well with observed data. The theoretical approach is similar to that of M. H. Cohen and J. Ruvalds, Phys. Rev. Letters 23, 1378 (1969).

[4]D. L. Rousseau and S. P. S. Porto, Phys. Rev. Letters 20, 1354 (1968). Green's function techniques have also been applied to the kind of anharmonic interactions discussed here, most notably by R. Cowley, Advan. Phys. 12, 421 (1963), and Proc. Phys. Soc. (London) 87, 281 (1964), and in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Plenum, New York, 1966), p. 170. A related treatment is given by A. S. Barker and J. J. Hopfield, Phys. Rev. 135, A1732 (1964).

[5]U. Fano, Phys. Rev. 124, 1866 (1961).

[6]E. Burstein, S. Ushioda, A. Pinczuk, and J. F. Scott, in *Light Scattering Spectra of Solids*, edited by G. Wright (Springer, New York, 1969), p. 43.

[7]M. M. Elcombe, Proc. Phys. Soc. (London) 91, 947 (1967).

[8]A. Zawadowski and J. Ruvalds, following Letter [Phys. Rev. Letters 24, 1111 (1970)].

[9]The most recent study of the α-β phase transition in $AlPO_4$ is that of R. Lang, W. R. Datars, and C. Calvo, Phys. Letters 30A, 340 (1969).

[10]A. Leadbetter, private communication, cited in Scott, Ref. 2.