Rev. Mod. Phys. 40, 380 (1968).
[2]P. W. Anderson, Phys. Rev. 124, 41 (1961).
[3]N. Rivier, M. J. Zuckermann, and M. Šunjić, to be published.
[4]J. R. Schrieffer, J. Appl. Phys. 38, 1143 (1967).
[5]P. W. Anderson, to be published.
[6]A. A. Abrikosov, Physics 2, 5 (1965).
[7]H. Suhl and D. Wong, Physics 3, 17 (1967).
[8]Y. Nagaoka, Progr. Theoret. Phys. 37, 13 (1967); H. J. Spencer, Phys. Rev., to be published.
[9]The concept of replacing a localized spin by localized spin fluctuations was first introduced by H. Suhl, Phys. Rev. Letters 19, 442 (1967). Computer calculations of the susceptibility and resistivity were reported in the above reference as well as in M. J. Levine and H. Suhl, Phys. Rev. 171, 567 (1968), and M. J. Levine, T. V. Ramakrishnan, and R. A. Weiner, Phys. Rev. Letters 20, 1370 (1968). They exhibit the change of regime discussed above and agree qualitatively with our results.
[10]Y. Nagaoka, Phys. Rev. 138, 1112 (1965), and J. Phys. Chem. Solids 27, 1139 (1966).
[11]J. Kondo, to be published.
[12]K. Kume, to be published.
[13]G. Boato and J. Vig, Solid State Commun. 5, 649 (1967).
[14]C. P. Flynn, D. A. Rigney, and J. A. Gardner, Phil. Mag. 15, 1255 (1967).
[15]A. D. Caplin and C. Rizzuto, to be published.
[16]E. Daniel and J. Friedel, in Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964, edited by J. G. Daunt (Plenum Press, New York, 1965) p. 933.
[17]J. A. Careaga, B. Dreyfus, R. Tournier, and L. Weil, in Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, U.S.S.R., 31 August-6 September 1966 (Vimiti Publishing House, Moscow, U.S.S.R., 1967).
[18]L. Dworin, Phys. Rev. 164, 818, 841 (1967). Dworin's high temperature results are formally similar to ours (Ref. 3). His "nonanalytic part" $\Gamma(T)$ is our spin fluctuation width τ^{-1} which is also nonanalytic in Δ (see the condition for the existence of a spin fluctuation). As Dworin considers an alloy in the Schrieffer-Wolff limit ($U \gg \Delta$), his $[\Gamma(T)]^{-1}$ might well be the suitably renormalized lifetime of the present theory. [See N. Rivier, thesis, University of Cambridge, (1968).]
[19]M. D. Daybell and W. A. Steyert, Phys. Rev. 167, 536 (1958).
[20]K. Yosida, Phys. Rev. 106, 893 (1957).
[21]J. R. Schrieffer and D. C. Mattis, Phys. Rev. 140, A1412 (1965).
[22]Our results agree with the predictions of Nagaoka. An exact solution of Nagaoka's approximate equations however, gives different results but leads to physical difficulties. [P. E. Bloomfield and D. R. Hamann, Phys. Rev. 164, 856 (1967); J. Zittartz and S. Müller-Hartmann, to be published.]

EVIDENCE OF COUPLING BETWEEN ONE- AND TWO-PHONON EXCITATIONS IN QUARTZ

J. F. Scott
Bell Telephone Laboratories, Holmdel, New Jersey
(Received 8 July 1968)

We have extended earlier work on the Raman spectrum of quartz to both higher and lower temperatures (6-900°K), and find evidence for the assignment of features in the 130- to 200-cm^{-1} region as second order. Anomalies in the temperature dependence and selection rules exhibited by several features are fully reconciled by an anharmonic interaction between a "soft" zone-center optical phonon and an excitation consisting of two oppositely directed zone-edge acoustic phonons.

The α-β phase transition in quartz has been approached by several investigators in terms of lattice dynamics. The analyses of Ginzburg and Levanyuk,[1] of Elcombe,[2] and of Kleinman and Spitzer[3] are similar, and each elaborates on the basic conclusion of Saksena's early force-constant calculation[4]: that the frequency of the 207-cm^{-1} mode (in this paper vibrations will be labeled by their frequencies at 300°K) at the Brillouin zone center should approach zero as the transition temperature T_0 is approached from below. Phenomenologically this behavior is not different from that of the ferroelectric mode in Cochran's theory,[5] except that the phonon in question is infrared inactive and does not directly contribute to the dielectric response of the crystal. The difficulty encountered by those who have attempted to apply existing theories to the quartz transition is that the experimental data simply do not confirm the predictions. First, the 207-cm^{-1} mode softens but does not approach zero as $T \to T_0$,[4] in contradiction to Ginzburg's requirement for second-order transitions.[6] Second, there is an extra Raman feature[7] in the α_{xx} and α_{zz} scattering in addition to the four predicted by group theory and assigned by means of force-constant models.[2,3] Third, the frequency of this "extra" feature does approach zero frequency as T approaches T_0 from

below.[8] Fourth, the 207-cm^{-1} mode, which has softened to 165 cm^{-1} at temperatures slightly less than T_0, remains undiminished in Raman scattering intensity and unchanged in frequency as the crystal goes through T_0, in defiance of the β-quartz selection rules, which require that it be Raman inactive.[9]

The extra feature referred to above occurs at 147 cm^{-1} at 300°K and was summarily dismissed as "not one of the eight fundamental (nondegenerate) vibrations" in a paper by Professor Porto and myself which reviewed the Raman work on quartz.[10] Cummins et al. have opposed the assignment of this feature as second order, however, and have suggested a model in which the 147- and 207-cm^{-1} excitations are both one-phonon processes; their identification of these features as due to quanta of a double-well potential[9] was based to some extent on their earlier report that the 147-cm^{-1} line grew out of the 207-cm^{-1} line as a shoulder at elevated temperatures, and that only a single unsplit line was present at 300°K.[8] In fact, while the 147-cm^{-1} line is considerably weaker at temperatures of 300°K and less, it is still present, as shown here and by our earlier work.[10]

Figure 1 shows the quartz spectrum from 130 to 200 cm^{-1} at several temperatures. At low temperatures the feature peaking at 147 cm^{-1} manifests its second-order character in that it is broad, asymmetric, and has several maxima. At temperatures of 300°K and above these characteristics are washed out for reasons discussed below. A second indication that the 147-cm^{-1} excitation is second order is that it was not observed in Miss Elcombe's neutron scattering work,[2] although a search of that frequency range was made and detailed the dispersion of the 128- and 207-cm^{-1} zone-center modes.

It is the intent of the present Letter to explain the unusual temperature dependence and selection rules exhibited by the Raman features discussed above as due to coupling between one- and two-phonon excitations. The 207-cm^{-1} feature is interpreted as a soft optic phonon and is considered to go to zero frequency at $T_0 = 573$°C. The feature peaking at 147 cm^{-1} is interpreted as excitation of two zone-edge acoustic phonons, and is viewed as intrinsically temperature independent. As the crystal is heated above 300°K, the soft optic phonon traverses the two-phonon continuum; the optic mode couples anharmonically to part of the two-phonon continuum—relaxation into certain acoustic phonon pairs has a very high probability—and an "anticrossing" characteristic of resonance between two coupled oscillators occurs. Since this anharmonic resonance is between the two-phonon state of one normal mode and the one-phonon state of a second, it is strikingly analogous to Fermi resonance in gas molecules such

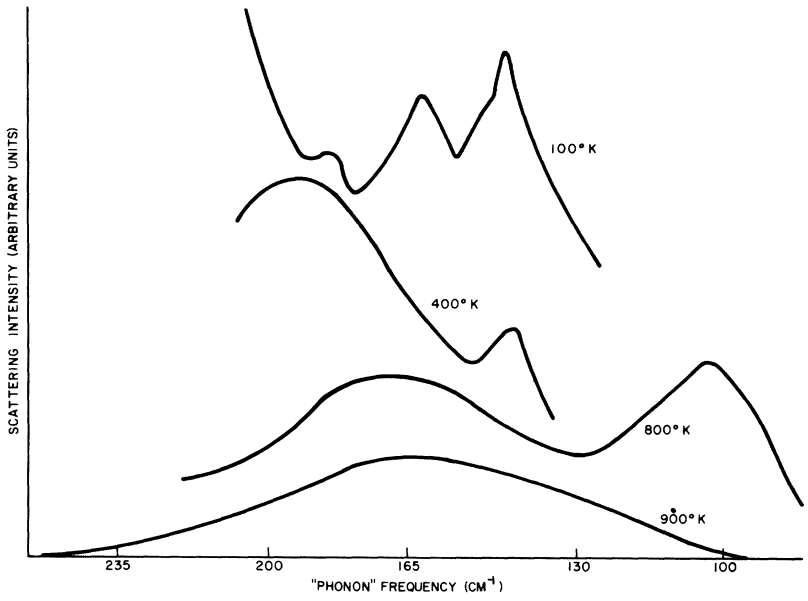

FIG. 1. Relative intensities of some α_{zz} Raman-scattering features in quartz. Scattering geometry was that of [100] laser photon, [010] Stokes wave, and [1$\bar{1}$0] phonon. The low-temperature features are of lower intensity and are shown on an enlarged scale (~×20). Excitations are referred to as "phonons" although they are anharmonic.

as H_2O, where the overtone of one mechanical vibration is near in frequency to the fundamental of another mode.

Figure 2 is a plot of the temperature dependence of features having frequencies of 207 and 147 cm^{-1} at 300°K. The solid lines represent the dependences expected for uncoupled excitations. The data points may be fitted to a good approximation by the equation $\omega(\pm) = \frac{1}{2}(\omega_1 + \omega_2) \pm \frac{1}{2}\{4|W_{12}|^2 + (\omega_1 - \omega_2)^2\}^{1/2}$ using the parameters $\omega_1 = 26(846°K - T)^{1/3}$ cm^{-1} $°K^{-1/3}$, $\omega_2 = 160$ cm^{-1} = const, and $|W_{12}|^2 = (1|H|2)(2|H|1) = \alpha\lambda(T)$. H designates the anharmonic vibrational Hamiltonian, $|1)$ and $|2)$ designate the one- and two-phonon states, $\lambda(T)$ is the experimental linewidth of the more intense of the two spectral features (assumed proportional to the anharmonicity), and $\alpha = 3$ cm^{-1}. It is to be noted that at very high or very low temperatures the feature in the region 130-170 cm^{-1} is essentially a two-phonon excitation. At intermediate temperatures it is a mixed excitation not easily described by the use of phonons. The interaction between the one- and two-phonon states is presumably by means of the large anharmonic terms in the Hamiltonian, which are evidenced by the extreme linewidth of the 207-cm^{-1} mode. At 300°K the coupling is sufficiently strong to enhance the Raman scattering from the 147-cm^{-1} excitation and to give this feature a more symmetric appearance. Above T_0 the excitation at

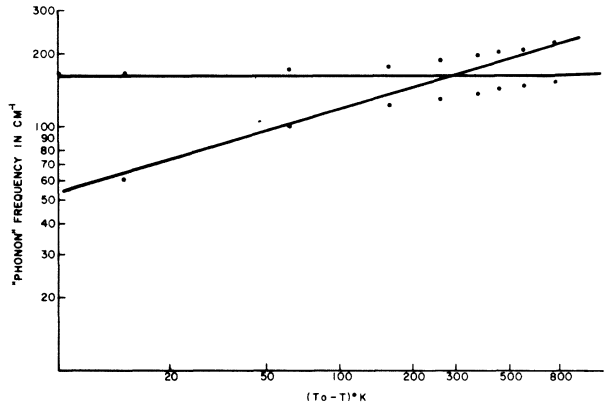

FIG. 2. Temperature dependences of the frequencies of two Raman features in quartz. The solid lines represent dependences expected for uncoupled excitations. This log-log plot of the data fits the equation $\omega_1 = A(T_0 - T)^n$ with $n = 0.30 \pm 0.05$. This is about the same value as we obtained for soft modes triggering the 110°K phase transition in $SrTiO_3$ [P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters 21, 16 (1968)], and shows that force constants are not linearly dependent on $T_0 - T$.

165 cm^{-1} is essentially second order and hence does not violate Raman selection rules. The soft optic mode is expected to harden again above T_0, but is infrared and Raman inactive, and attempts to detect it via neutron scattering have not yet been successful.[2]

The assignment of the 147-cm^{-1} feature as due to two zone-edge acoustic phonons is furthered by the information[11] that neutron scattering from polycrystalline quartz exhibits a peak at 70 ± 5 cm^{-1}. [Miss Elcombe's neutron studies on quartz monocrystals[2] detailed only (001) propagation.] Consequently, the 147-cm^{-1} feature is to be viewed as an overtone, rather than a combination band.

Finally, the observation that the two-acoustic-phonon density of states peaks at ~147 cm^{-1} at 300°K and below helps to explain the narrow linewidth of the E symmetry mode at 128 cm^{-1} (which is, not coincidentally, the only infrared-active vibration yet discovered to produce stimulated Raman scattering[12]); relaxation into two or more acoustic phonons is forbidden by symmetry considerations over that part of the Brillouin zone where the density of states is greatest.[13]

In conclusion, the 147-cm^{-1} excitation is assigned as two zone-edge acoustic phonons, and the anomalous frequency and intensity dependences upon temperature are interpreted in terms of an interaction between one- and two-phonon excitations similar to that invoked by others to explain features in the $BaTiO_3$ spectrum[14] and described by them as an Auger-like process.

The author wishes to express his appreciation to Professor J. J. Hopfield, who suggested the coupled-excitation model and made other helpful comments, and to Dr. J. M. Worlock for several educational discussions. Thanks are also due L. E. Cheesman and T. C. Damen, who recorded the Raman data presented in Figs. 1 and 2.

[1]V. L. Ginzburg and A. P. Levanyuk, Zh. Eksperim. i Teor. Fiz. 39, 192 (1960) [translation: Soviet Phys. – JETP 12, 138 (1961)].

[2]Margaret M. Elcombe, dissertation, Cambridge University, 1966 (unpublished), and Proc. Phys. Soc. (London) 91, 947 (1967).

[3]D. A. Kleinman and W. G. Spitzer, Phys. Rev. 125, 16 (1962).

[4]B. D. Saksena, Proc. Indian Acad. Sci., Sec. A 12, 93 (1940); B. D. Saksena and H. Narain, ibid. 30, 128 (1949); see also J. Barriol, J. Phys. Radium 7, 209 (1946).

[5]W. Cochran, Advan. Phys. 10, 401 (1961).

[6]V. L. Ginzburg, Fiz. Tverd. Tela 2, 2031 (1960) [translation: Soviet Phys.—Solid State 2, 1824 (1960)].
[7]R. S. Krishnan, Proc. Indian Acad. Sci., Sec. A 22, 329 (1945); D. Krishnamurti, ibid. 47, 276 (1958).
[8]S. M. Shapiro and H. Z. Cummins, Bull. Am. Phys. Soc. 12, 588 (1967).
[9]S. M. Shapiro, D. C. O'Shea, and H. Z. Cummins, Phys. Rev. Letters 19, 361 (1967).
[10]J. F. Scott and S. P. S. Porto, Phys. Rev. 161, 903 (1967).
[11]Thanks are due to Professor A. J. Leadbetter, University of Bristol, for this unpublished information.
[12]P. E. Tannenwald and D. L. Weinberg, J. Quantum Electron. 3, 334 (1967).
[13]Pointed out by Professor S. P. S. Porto, private communication.
[14]D. L. Rousseau and S. P. S. Porto, Phys. Rev. Letters 20, 1354 (1968).

EXCITON-MAGNON INTERACTION IN MAGNETIC INSULATORS

S. Freeman
RCA Laboratories, Princeton, New Jersey

and

J. J. Hopfield*
Princeton University, Princeton, New Jersey
(Received 10 July 1968)

The one-exciton, one-magnon system is treated for a suitable antiferromagnetic insulator, MnF_2. Zone-edge excitons and magnons are found to interact quite strongly. Bound states are found to exist under favorable circumstances. The line shapes of magnon sidebands of excitonic transitions are modified. Expressions are given for the exciton-magnon coupling constants in terms of the parameters describing interionic exchange.

We have studied the one-exciton, one-magnon system in an antiferromagnetic insulator. Interionic exchange (including superexchange) provides the major source of interaction between these excitations. Approximations of the type customary in dealing with antiferromagnets reduce the many-body problem to a two-particle scattering problem; the latter has a simple structure permitting explicit solution. The extent to which interaction modifies the dominant features of the magnon sideband of the excitonic transition can then be displayed. The most dramatic effect is the existence of bound states below or above the two-particle continuum when certain conditions are satisfied.[1]

We have concentrated particularly on the magnon sideband of the lower ${}^6A_1 \rightarrow ({}^4A_1, {}^4E_\theta)$ absorption line in MnF_2. In this we were motivated by the description of preliminary experimental results most kindly provided by D. S. McClure and R. S. Meltzer. Their results indicate a large, negative exciton dispersion in the c direction. The sideband peak corresponding to constituent Z-point excitations thus lies some 19 cm^{-1} below the zero-magnon line, while the presence of an additional split-off component 1.6 cm^{-1} lower still suggests the presence of a bound state.[2]

The exciton state considered has the same orbital occupancy as the ground state. This ensures that coupling to lattice distortions is unimportant. Moreover, it is easily shown that the coupling of the exciton to adjacent spins through a direct Coulomb interaction plus spin-orbit coupling is small compared with typical exchange energies. On the other hand, Anderson's expression for the interionic exchange,[3] which is expressed as a sum of contributions from electrons occupying individual orbitals (more strictly, Wannier states) centered on adjoining sites, gives rise directly to exciton dispersion and to exciton-magnon coupling comparable in magnitude with exchange energies in the ground state (~50 cm^{-1}). Each of the interaction terms coupling a pair of sites i and j has the form of a scalar product of operators which transform as spin vectors at the two sites. One such interaction term is the usual exchange $\vec{S}^{(i)} \cdot \vec{S}^{(j)}$. It will suffice to consider only nearest-neighbor (n.n.) pairs (same sublattice) and next nearest (n.n.n.) (opposite), since only they have nonzero exchange constants in the ground state. The exchange constant is modified if a site is occupied by an exciton. We write the modified exchange constants J_1' for nearest and J_2' for next-nearest neigh-