Casella, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors*, edited by S. M. Ryukin (Nauka, Leningrad, 1968).
[8]H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, Phys. Rev. 143, 648 (1966).
[9]O. N. Tufte and E. L. Stelzer, Phys. Rev. 173, 775 (1968).
[10]K. W. Blazey, Phys. Rev. Letters 27, 146 (1971).
[11]N. E. Phillips, B. B. Triplett, R. D. Clear, H. E. Simon, J. K. Hulm, C. K. Jones, and R. Mazelsky, in *Proceedings of the International Conference on the Science of Superconductivity*, edited by F. Chilton (North-Holland, Amsterdam, 1971).
[12]K. A. Müller, W. Berlinger, M. Capizzi, and H. Gränicher, Solid State Commun. 8, 549 (1970).
[13]G. F. Koster, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957).
[14]P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters 21, 16 (1968).
[15]G. Shirane and Y. Yamada, Phys. Rev. 177, 858 (1969); R. A. Cowley, W. J. L. Buyers, and G. Dolling, Solid State Commun. 7, 181 (1969).
[16]J. R. Brews, Phys. Rev. Letters 18, 662 (1967).
[17]B. C. Frazer, H. R. Danner, and R. Pepinsky, Phys. Rev. 100, 745 (1955).
[18]J. D. Zook and T. N. Casselman, Phys. Rev. Letters 17, 960 (1966).
[19]C. N. Berglund and W. S. Baer, Phys. Rev. 157, 358 (1967).
[20]C. K. Jones and J. K. Hulm, Phys. Letters 26A, 182 (1968); D. W. Deis, J. K. Hulm, and C. K. Jones, Bull. Am. Phys. Soc. 14, 61 (1969); D. W. Deis, M. Ashkin, J. K. Hulm, and C. K. Jones, *ibid.* 15, 102 (1970).
[21]N. E. Phillips, J. C. Ho, D. P. Woody, J. K. Hulm, and C. K. Jones, Phys. Letters 29A, 356 (1969).
[22]E. Ambler, J. H. Colwell, W. R. Hosler, and J. F. Schooley, Phys. Rev. 148, 280 (1966).
[23]H. P. R. Frederikse, W. R. Hosler, W. R. Thurber, J. Babiskin, and P. G. Siebenmann, Phys. Rev. 158, 775 (1967).
[24]D. Redfield and W. J. Burke, Phys. Rev. Letters 28, 435 (1972).
[25]S. H. Wemple, Phys. Rev. B 2, 2679 (1970).
[26]M. Capizzi and A. Frova, Nuovo Cimento 5B, 181 (1971).
[27]C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. 163, 380 (1967).
[28]M. L. Cohen, Phys. Rev. 134, A511 (1964).
[29]J. Appel, Phys. Rev. 180, 508 (1969).
[30]Z. Zinamon, Phil. Mag. 21, 347 (1970).
[31]E. R. Pfeiffer and J. F. Schooley, J. Low Temp. Phys. 2, 333 (1970).
[32]W. J. Burke and R. J. Pressley, Solid State Commun. 9, 191 (1971).

PHYSICAL REVIEW B VOLUME 6, NUMBER 12 15 DECEMBER 1972

Raman Scattering, Luminescence, and Exciton-Phonon Coupling in Cu_2O†

A. Compaan and H. Z. Cummins*
Department of Physics, New York University, New York, New York 10003
(Received 29 June 1972)

Raman scattering and exciton luminescence and absorption have been studied in high-purity single-crystal Cu_2O at liquid-helium temperature using 4880-Å laser excitation. The Raman-active mode has been unambiguously identified at 515 cm^{-1}, and the first observation made of luminescence from the $n=2$, 3, 4 yellow excitons and their continuum. Comparison of the Raman spectra with the absorption and luminescence spectra near the $n=1$ exciton has clarified the origin of the strong 220-cm^{-1} Raman feature and yielded evidence for wave-vector-independent and wave-vector-dependent exciton-phonon coupling, respectively, for the Γ_{12}^- and Γ_{15}^- optic phonons.

INTRODUCTION

In this paper we present the results of Raman scattering and laser-excited recombination luminescence from the yellow exciton series[1–3] in cuprous oxide Cu_2O. These measurements have allowed us to unambiguously identify at 515 cm^{-1} the Γ_{25}^+ Raman-active mode whose frequency has previously been reported as 220, 197, and 598 cm^{-1} by various groups.[4–6] We have also observed for the first time the direct recombination radiation from the $n=2$, 3, 4 and higher exciton states and from the series continuum. Comparison of the Raman spectra with the phonon-assisted 1S exciton luminescence has clarified the origin of other features of the Raman spectrum, such as the strongest peak at 220 cm^{-1} which we identify as scattering from two 110-cm^{-1} phonons. Finally, digital measurements of phonon-assisted 1S exciton absorption have indicated that the exciton-phonon coupling is independent of the phonon wave vector q for the Γ_{12}^- phonon but linear in q for the Γ_{15}^- phonon.

Our experiments were performed on a 1-mm-thick slice from a large single-crystal Cu_2O boule grown by Brower and Parker[7] by a floating-zone technique. Forman, who has studied the optical absorption of these crystals,[8] provided

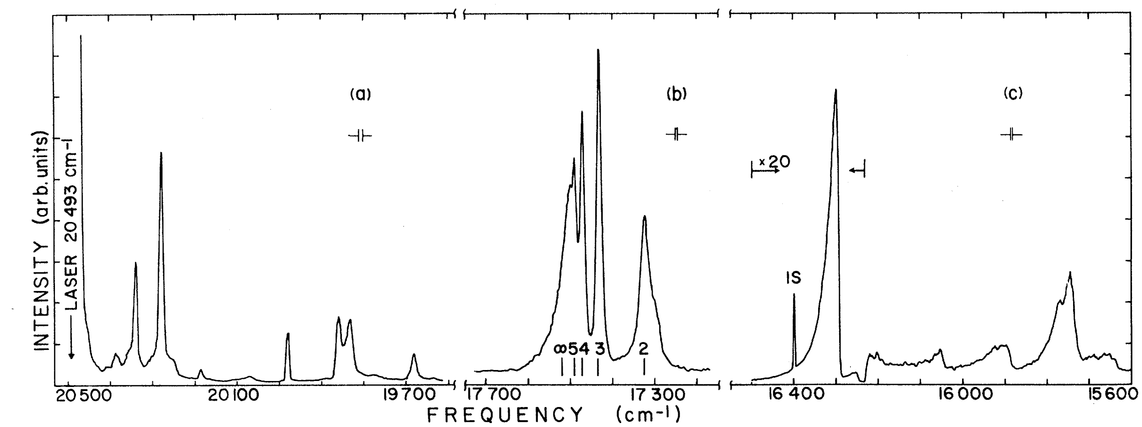

FIG. 1. Light scattering and luminescence spectrum of Cu_2O obtained with 50 mW of 4880-Å laser excitation at 4.2 °K showing (a) the Raman spectrum, (b) excited-state exciton luminescence, and (c) 1*S* exciton luminescence with phonon sidebands, as discussed in the text. The gain in region (c) from 16 500 to 16 230 cm^{-1} is a factor of 20 lower than in the remainder. The instrumental resolution is indicated by the vertical bars.

us with the sample. The experiments employed He-Ne and Ar^+ lasers, a Spex 1401 double-grating spectrometer, and photon-counting electronics. The crystal was mounted on a copper stud within a helium Cryotip Dewar, [9] and surrounded with helium exchange gas.

A representative spectrum[10] obtained with 50 mW of 4880-Å excitation is shown in Fig. 1. Scanning down in frequency from the laser line, three groups of features are seen: In the first 1000 cm^{-1} the Raman spectrum occurs; near 17 500 cm^{-1} we observe recombination luminescence from the continuum and excited states of the yellow exciton series; at 16 400 cm^{-1} the sharp zero-phonon 1*S* luminescence occurs, followed by a series of phonon-assisted 1*S* luminescence features some of which have been previously discussed by Gross.[3,11]

RAMAN MODE

Cuprous oxide has six zone-center optic phonons of which the two infrared-active Γ_{15}^- modes are known from infrared-absorption and reflectivity data[12] with TO and LO frequencies of 143 and 160 cm^{-1} and 608 and 640 cm^{-1}; the frequency of the Γ_{12}^- mode is known from phonon-assisted absorption and luminescence as 110 cm^{-1}.[13] Rigid-ion-lattice-dynamics calculations by Carabatos and Prevot[14] predict that the remaining three modes are Γ_{25}^- (99 cm^{-1}), Γ_2^- (307 cm^{-1}), and Γ_{25}^+ (550 cm^{-1}). Of the six, only the Γ_{25}^+ mode should be Raman-active in single-phonon scattering; however, its frequency and polarization properties have not been clearly identified experimentally in spite of several attempts.[4–6] Our Raman-scattering measurements were performed in a back-scattering geometry from a (101) face. In Fig. 2 traces (a) and (b) show the spectra obtained with (y, y) and $(y, -x+z)$ polarizations, respectively, with 4880-Å excitation. The 515-cm^{-1} peak is missing in the diagonal trace (a), but dominates the off-diagonal

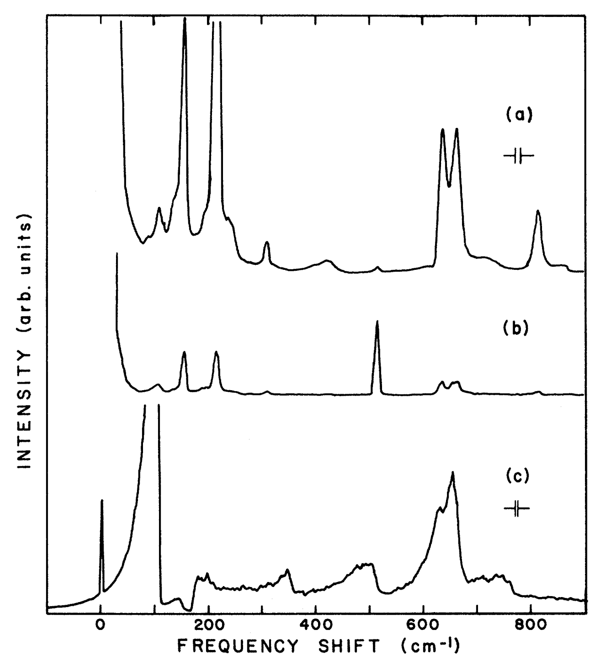

FIG. 2. Traces (a) and (b): Raman scattering spectra of Cu_2O obtained with 50 mW at 4880 Å for normal incidence along a (101) direction. Incident and scattered polarizations: (y, y) for trace (a) and $(y, -x+z)$ for trace (b). Instrumental resolution of 9 cm^{-1} is indicated. Trace (c): phonon-assisted 1*S* luminescence spectrum with the zero-phonon 1*S* quadrupole emission line aligned with the laser frequency in traces (a) and (b). Instrumental resolution was 4 cm^{-1} for this trace. The crystal was at liquid-helium temperature.

trace (b) in agreement with the scattering tensor for the Γ_{25}^{+} phonon. We therefore identify the 515-cm^{-1} peak as the Γ_{25}^{+} Raman-active mode. The observed frequency compares reasonably with the 550 cm^{-1} prediction of Carabatos and Prevot.[14] We have found that it is much weaker with 5145-Å excitation and nearly undetectable with 6328-Å excitation of equivalent power, which may account for its previous elusiveness.

PHONON-ASSISTED EXCITON LUMINESCENCE

Zero-phonon radiative recombination from S states of the yellow series is dipole forbidden because the electron and hole arise from conduction and valence bands of the same parity—conduction band Γ_1^{+} and valence band Γ_{25}^{+} (neglecting spin-orbit splitting). The zero-phonon line occurs in quadrupole emission; however, it can readily be shown[13] that all the odd-parity phonons can participate in phonon-assisted electric dipole radiation from the 1S. Thus the 1S-phonon sideband luminescence is completely complementary to Raman scattering in terms of allowed phonon participation. We have plotted in Fig. 2(c) the luminescence spectrum directly under the Raman spectra with the 1S position in luminescence aligned with the laser frequency in Raman scattering. For a particular sideband, the displacement of the low-frequency edge from the 1S may be taken as the frequency of the participating phonon. (Line shapes of the phonon sidebands are discussed below.) The luminescence spectrum is dominated by the 110-cm^{-1} Γ_{12}^{-} phonon, with weaker edges appearing at 150, 350, and 515 cm^{-1}, and a double peak with edges at approximately 630 and 660 cm^{-1}. The edge at 350 cm^{-1} probably corresponds to the Γ_2^{-} phonon, again in reasonable agreement with the calculated frequency of 307 cm^{-1}, while the 150-cm^{-1} edge and the double peak correspond to the two ir active Γ_{15}^{-} modes. The 515-cm^{-1} edge appears to correspond to the Raman mode although nominally forbidden.

Comparison of the Raman spectra with the exciton-phonon luminescence spectrum suggests that the strong, narrow ($\Delta\bar{\nu} \simeq 5$ cm^{-1}) 220-cm^{-1} Raman feature is second-order scattering from the 110-cm^{-1} Γ_{12}^{-} phonon for the following reasons: The exciton luminescence spectrum is dominated by the 110-cm^{-1} phonon sideband, indicating that it is more strongly coupled to the excitons than any of the other phonons. Furthermore, in calculations of Carabatos and Prevot the Γ_{12}^{-} mode has an extremely flat dispersion curve, giving rise to a large narrow peak in the two-phonon density of states. Thus the 220-cm^{-1} line derives its strength from the coincidence of the high density of states and the strong exciton-phonon coupling.[15] The two-phonon explanation was previously suggested by Carabatos and Prevot,[14] and may also apply to the 308-cm^{-1} Raman feature, identified then as two-phonon scattering by the 150-cm^{-1} mode which gives the second strongest sideband in the exciton-phonon luminescence spectrum. Further comparison shows that the observed Raman features at 110, 158, 640, and 660 cm^{-1} correspond closely to the frequencies of odd-parity phonons, and are thus presumably impurity-activated intrinsic phonons as discussed by Balkanski *et al.*[6]

EXCITON-PHONON COUPLING

We have further explored the coupling of 1S excitons to optical phonons both in absorption and luminescence. At 4 °K the 1S exciton appears weakly in direct quadrupole absorption at 16 400 cm^{-1}. Continuous phonon-assisted absorption begins 110 cm^{-1} above the 1S line with the creation of zone-center Γ_{12}^{-} phonons and 1S excitons. With increasing frequency, excitons are created with $\vec{q} \neq 0$ by simultaneous emission of a phonon of wave vector $\vec{q}\,' = \vec{k} - \vec{q}$, where $\vec{k}$ is the photon wave vector. The absorption constant α is proportional to the strength of the exciton-phonon coupling, and to the density of states $[E(\vec{q}) - E(\vec{q}=0)]^{1/2}$, which assumes only that the combined exciton plus phonon energy is proportional to q^2. Next, at 150 cm^{-1} above the 1S line, the Γ_{15}^{-} phonon may contribute additional absorption, etc.

Figure 3 shows our absorption data at 4 °K which were obtained with the double-grating spectrometer employing a white-light source and digital data recording and analysis. The best fit for the absorption constant over the range from the edge out to ~ 550 cm^{-1} using the 110- and 150-cm^{-1} phonons which dominate the luminescense spectrum is given by

$$\alpha(\bar{\nu} - \bar{\nu}_{1S}) = 0.034\,(\Delta\bar{\nu} - 110)^{1/2} + 1.3\times 10^{-5}(\Delta\bar{\nu} - 150)^{3/2}\ \text{cm}^{-1}\ , \quad (1)$$

where $\Delta\bar{\nu} = \nu - \nu_{1S}$. Each of the two contributions to the absorption constant is shown separately in Fig. 3 together with their sum. Note that the contribution from the 150-cm^{-1} phonon contains an extra factor of $(\Delta\bar{\nu} - 150)$. This result can be understood on the basis of available intermediate states such as the nearest conduction band[16] of symmetry Γ_{12}^{-} for which phonon-assisted absorption would be permitted for Γ_{12}^{-} phonons but not for Γ_{15}^{-} phonons. Absorption involving the 150-cm^{-1} Γ_{15}^{-} phonons could then occur only for $q \neq 0$ with a (lowest-order) linear q dependence in the matrix element or a q^2 dependence of the transition probability; consequently, an extra factor of $(\Delta\bar{\nu} - 150)$ arises in the absorption constant.[17] We note, however, that this analysis neglects a small intrinsic frequency dependence of the transi-

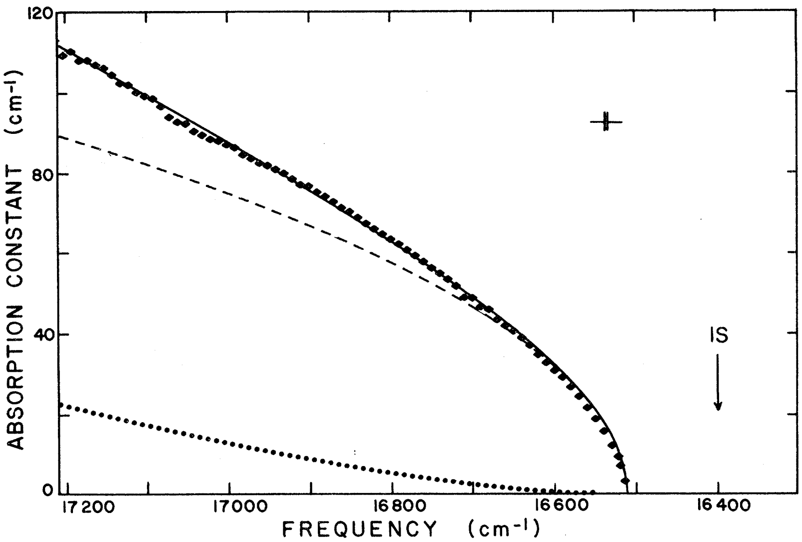

FIG. 3. Absorption constant of Cu_2O as a function of frequency. The arrow at 16 400 cm^{-1} indicates the direct 1S quadrupole absorption; phonon-assisted absorption begins above 16 510 cm^{-1}. The solid curve is a fit to the data discussed in the text; the dashed and dotted curves show, respectively, the contributions of the 110-cm^{-1} and 150-cm^{-1} phonons. For clarity only every fifth data point was plotted; instrumental resolution was 3 cm^{-1}.

tion probabilities associated with energy denominators, as well as possible contributions to absorption from other phonons.

We have also employed digital data recording techniques to study the line shape of the 110-cm^{-1} sideband in the 1S luminescence spectrum. In this case, the shape depends on the density of states and the exciton-phonon coupling constant just as in absorption, but there is also a statistical factor giving the number of excitons per state. Thus, one obtains for the radiated intensity

$$I(\Delta\bar{\nu}) = I_0(\Delta\bar{\nu})^{1/2}\,(e^{(\Delta\bar{\nu}-\mu)/kT^*} - 1)^{-1} , \qquad (2)$$

where $\Delta\bar{\nu}$ is the frequency in cm^{-1} above the 110-cm^{-1} edge, T^* is an effective exciton temperature, and the chemical potential μ is to be determined by normalization. For our experimental conditions we estimate an upper limit for the 1S exciton density of 10^{14} cm^{-3}, which places μ at least 15 cm^{-1} below the bottom of the 1S band for $T^* \geq 4$ °K. In this case the Bose–Einstein factor in Eq. (2) is indistinguishable from the classical Maxwell–Boltzmann distribution previously employed by Gross.[3,11] Our measured line shapes fit Eq. (2) reasonably well, but indicate a systematic difference of ~10 °K between the effective exciton temperature T^* and the lattice temperature, and some excess intensity in the high-frequency portion of the band. The effective exciton temperature T^* was not less than ~15 °K even with laser power of 5 mW, indicating that the net lifetime for 1S excitons is too short to permit complete thermalization to occur.

Finally, we comment briefly on the excited-state exciton luminescence shown in Fig. 1. The $n = 2$ emission line is asymmetric, but the asymmetry is significantly less than has been inferred on the basis of absorption data[18] where the measurement is complicated by the continuum from the 1S phonon-assisted absorption. The luminescence asymmetry may be explained in terms of a 2S-2P splitting of about 25 cm^{-1} which might arise from central-cell corrections in the S states.

ACKNOWLEDGMENTS

We wish to thank Professor J. Birman, Dr. R. Zeyher, Professor R. J. Elliott, and Dr. R. A. Forman for many helpful discussions on the theory of Cu_2O, and Dr. R. A. Forman, W. S. Brower, Jr., and H. S. Parker of the National Bureau of Standards for making their crystal available to us.

---

†Work supported by the National Science Foundation.
*Alfred P. Sloan Research Fellow.

[1]E. F. Gross, Usp. Fiz. Nauk 63, 575 (1957) [Advan. Phys. Sci. (USSR) 63, 782 (1957)]; E. F. Gross, *ibid.* 76, 433 (1962) [Sov. Phys. Usp. 5, 195 (1962)], and references therein.

[2]S. Nikitine, in *Optical Properties of Solids*, edited by Nudelman and Mitra (Plenum, New York, 1969), p. 197; J. L. Deiss, A. Daunois, and S. Nikitine, Phys. Status Solidi (b) 47, 185 (1971), and references therein.

[3]E. F. Gross, S. A. Permogorov, and B. S. Razbirin, Usp. Fiz. Nauk 103, 431 (1971) [Sov. Phys. Usp. 14, 104 (1971)].

[4]M. Balkanski, M. A. Nusimovici, and J. Reydellet, Solid State Commun. 7, 815 (1969).

[5]A. I. Stekhanov and Yu F. Markov, Fiz. Tverd. Tela 11, 3330 (1969) [Sov. Phys. Solid State 11, 2698 (1970)].

[6]M. Balkanski, J. Reydellet and D. Trivich (unpublished).

[7]W. S. Brower, Jr. and H. S. Parker, J. Cryst.

Growth 8, 227 (1971).

[8]R. A. Forman, W. S. Brower, Jr., and H. S. Parker, Phys. Letters 36A, 395 (1971).

[9]Air Products and Chemicals, Inc., Allentown, Pa.

[10]Following a suggestion of R. A. Forman that a surface layer of cupric oxide might be formed after several months exposure to air, we obtained additional Raman spectra immediately after etching the crystal with concentrated nitric acid. The spectra thus obtained were identical to those presented here.

[11]E. F. Gross, B. S. Razbirin, and S. A. Permogorov, J. Phys. Chem. Solids 27, 1647 (1966).

[12]I. Pastrniak, Opt. i Spektroskopiya 6, 64 (1959) [Opt. Spectry. (USSR) 6, 64 (1959)]; M. O'Keefe, J. Chem. Phys. 39, 1789 (1963); E. C. Heltemes, Phys. Rev. 141, 803 (1966); C. Carabatos, A. Diffine, and M. Sieskind, J. Phys. (Paris) 29, 529 (1968).

[13]R. J. Elliot, Phys. Rev. 124, 340 (1961).

[14]C. Carabatos and B. Prevot, Phys. Status Solidi (b) 44, 701 (1971).

[15]Definitive identification of the two-phonon nature of the 220-cm^{-1} peak via the temperature dependence of its intensity is complicated by possible resonant effects for the Ar^+ laser lines and the 6328-Å He-Ne laser transition [cf. M. Balkanski, J. Reydellet, and D. Trivich, Solid State Commun. 10, 1271 (1972)].

[16]J. P. Dahl and A. C. Switendick, J. Phys. Chem. Solids 27, 931 (1966); V. T. Agekyan, E. F. Gross, and A. A. Kaplanski, Fiz. Tverd. Tela 7, 781 (1965) [Sov. Phys. Solid State 7, 623 (1965)]; S. Brahms, and M. Cardona, Solid State Commun. 6, 733 (1968).

[17]The only other odd-parity band, the low-lying Γ_{15}^- valence band (see Ref. 16), appears not to be an important intermediate state since it would produce a q-independent exciton-phonon coupling for the Γ_{15}^- phonon.

[18]L. P. Zverev, M. M. Noskov, and M. Ya. Shur, Fiz. Tverd. Tela 2, 2643 (1960) [Sov. Phys. Solid State 2, 2357 (1960)]; S. Nikitine, J. B. Grun, and M. Sieskind, J. Phys. Chem. Solids 17, 292 (1961); A. Daunois, J. C. Merle, J. L. Deiss, and S. Nikitine, Phys. Status Solidi (b) 50, 691 (1972).

PHYSICAL REVIEW B VOLUME 6, NUMBER 12 15 DECEMBER 1972

Phonon-Radiation Force in Defect Crystal Lattices*

Richard S. Sorbello†

Department of Applied Physics, Stanford University, Stanford, California 94305

(Received 2 February 1972)

We derive expressions for the force exerted on any atom in a defect crystal lattice due to the scattering of phonons. This force is called the phonon-radiation force, and is essentially the microscopic counterpart of the radiation pressure in classical continuum mechanics; as such it finds its origins in lattice anharmonicity and is related to local thermal expansion. Although our analysis is entirely distinct from a pseudomomentum approach, we find that in the low-frequency limit the net phonon-radiation force on the entire crystal may be roughly approximated by associating with each phonon in mode $\vec{q}$ a momentum equal to the pseudomomentum $\hbar\vec{q}$. A calculation based on a one-dimensional chain reveals that the force field generally depends quite strongly on atomic position and is rather sensitive to the details of the scattering center. The phonon-radiation force does not appear to be important for vacancy migration, but should be important for other migration mechanisms.

I. INTRODUCTION

When a lattice wave is scattered by an impurity atom, it may exert a force on the impurity. General conservation laws can be derived to show that the sum of the momentum of the particle and the so-called pseudomomentum, or field momentum, of the wave system is a constant of motion.[1,2] The pseudomomentum is a fictitious wave momentum equal to the action of the wave divided by its wavelength,[2] or simply $\hbar\vec{q}$ for a quantum-lattice wave of wave vector $\vec{q}$. Pseudomomentum-based calculations of forces have been performed for liquid metals,[3] for liquid helium,[4] and recently for solids.[5] It is not clear, however, that a pseudomomentum calculation is actually valid for solids.[5,6] Our work indicates that in fact a pseudomomentum approach is not appropriate for defect scattering in crystalline solids, and that another approach is more meaningful—namely, one which is closely related to the concept of radiation pressure.

The problem with the usual pseudomomentum approach is that it assumes that the lattice and the impurity are separate entities and that momentum is a relevant quantity for an impurity atom in a crystal lattice. In reality, these assumptions are inappropriate because the impurity atom is not very mobile, but rather is strongly bound in the lattice system in more or less the same way as the regular lattice atoms. Consider, for example, phonon scattering by a mass-isotope impurity connected to its neighbors through some perturbed-harmonic linkages. From a simple pseudomomentum approach, each scattered phonon would contribute a nonzero force on the impurity equal to the change in pseudomomentum during the