retical work is shown in Fig. 1(b).[12] We note that the change in resistance represented by this curve is similar in magnitude and in field dependence to the dashed curve of our calculation in Fig. 1(a).

The dashed curve of $R(B)$ in Fig. 1(a) also resembles the anomaly observed in potassium. However, the experimental curve appears to be broader and shifted to higher fields. This may be attributed in part to a sloping background signal which is characteristic of an ordinary diffuse semiclassical calculation.[3] Such a background would not appear in our somewhat idealized treatment.

Although we have noted the similarity of our calculated curves to those of the rough-surface calculation, we would like to emphasize that our result is a purely quantum effect which arises naturally in a free-electron metal. In principle it should be possible to differentiate experimentally between the two interpretations; increasing τ by improving the metal surface should cause an increase in magnitude of the quantum effect, but a decrease in the semiclassical rough-surface effect.

One of us (J.F.C.) would like to thank G. A. Baraff and S. Schultz for stimulating discussions. We are both grateful to R. Barrie and A. V. Gold for helpful comments, and to the latter for financial support under a grant from the National Re-search Council of Canada.

[1]G. S. Baraff, C. C. Grimes, and P. M. Platzman, Phys. Rev. Lett. 22, 590 (1969).

[2]A similar broad signal has been observed in transmission through sodium slabs. G. L. Dunifer, thesis, University of California, San Diego, Calif. (unpublished), and S. Schultz (private communication).

[3]R. G. Chambers, Phil. Mag. 1, 459 (1956).

[4]M. I. Azbel' and M. I. Kaganov, Dokl. Akad. Nauk SSSR 95, 41 (1954).

[5]For anisotropic systems bandstructure effects can give rise to surface inpedance anomalies in a semiclassical calculation as discussed by V. P. Naberezhnykh and N. K. Dan'shin, Zh. Eksp. Teor. Fiz. 56, 1223 (1969) [Sov. Phys. JETP 29, 658 (1969)].

[6]P. B. Miller and R. R. Haering, Phys. Rev. 128, 126 (1962).

[7]G. A. Baraff, Phys. Rev. 187, 851 (1969).

[8]G. A. Baraff, Phys. Rev. B 1, 4307 (1970), and to be published.

[9]Our calculation does not concern the narrow peak of the Fermi-liquid theory. However, because of the resemblance between our calculated broad signal and that of Ref. 7, a similar enhancement is expected.

[10]R. E. Prange and T. W. Nee, Phys. Rev. 168, 779 (1968).

[11]A. P. van Gelder, Phys. Rev. 187, 833 (1969).

[12]The curve selected is representative of the size and shape of the anomaly as calculated in Ref. 7. However, by varying the available parameters somewhat arbitrarily, Baraff can obtain a more quantitative fit to experiment (see Fig. 7 of Ref. 7).

Ultraviolet Emission Spectra of Electron-Excited Solid and Liquid Neon

Richard E. Packard and F. Reif*

Physics Department, University of California, Berkeley, California 94720

and

C. M. Surko†

Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 22 September 1970)

The electron-excited emission spectrum of solid neon is found to be unique among the condensed rare gases in exhibiting a narrow atomiclike exciton line (located at 743 Å) In addition, the spectra of both solid and liquid neon show broad lines, probably attributable to radiation from Ne_2 molecules

In studying the electronic-excited states of solids and liquids, many investigators have turned their attention to the condensed phases of the rare-gas elements[1,2] since the simplicity of these substances should make them amenable to theoretical interpretation. Although the simplest, and thus most appealing, of these substances are helium and neon, these have heretofore not been studied because their investigation requires a difficult combination of cryogenic and vacuum-ultraviolet (v-uv) spectroscopic techniques. Solid helium presents almost insuperable obstacles since it exists only at pressures above 25 atm, an inaccessible domain since there exist no transparent windows in the far v-uv region. Liquid helium has very recently been studied by

reflection spectroscopy[3] and also by electron-excited luminescence.[4,5] Neon is thus the simplest rare-gas element which can be investigated in both the solid and liquid phases. The present paper reports such an investigation, by electron-excited luminescence, in the spectral region between 400 and 2000 Å.

The experimental apparatus is essentially the same as that previously used in measurements of the luminescence of liquid helium.[4] The chamber containing the condensed sample is maintained in weak thermal contact with a liquid-helium reservoir at 4.2°K. An electric heater attached to the sample chamber can raise its temperature to any point in the range between 12 and 60°K. The sample covers an electron emitter (a tritiated-titanium β source having an effective strength of 1 Ci) located at the bottom of the sample chamber. Ultraviolet radiation emanating from the electron-excited sample passes upward, without traversing any windows, through a monochromator located at the top of the apparatus.[6] It then impinges on a sodium salicylate converter where it produces visible light detected by a photomultiplier tube.

A fixed amount of neon gas[7] is introduced into the sample chamber after passing through a charcoal trap cooled to dry-ice temperature. This gas is cooled slowly (in about 4 h) from 77 to 12°K. Depending on the initial pressure of the gas, the solid neon is either formed by sublimation of the vapor (probably giving rise to a solid sample in the form of a snow) or by solidification of the liquid (giving rise to an annealed compact solid).

Our measurements on solid, liquid, and gaseous neon show spectral features only in the range between 700 and 1000 Å.[8]

The spectrum of solid neon is shown in Fig. 1. This spectrum consists of a relatively intense narrow line located at 743 ± 1 Å and having a full width at half-maximum (FWHM) less than 3.6 Å[9]; of a less intense peak at 774 Å (with FWHM = 20 ± 5 Å); and of a very faint broad hump near 890 Å (with FWHM = 40 ± 10 Å). The integrated intensities of these lines are, respectively, in the approximate ratios of 30:15:2. The shape of the spectrum is independent of sample thickness (in the range from 1 to 10 mm) and of temperature (in the range from 12 to 16°K). It is also independent of the method of sample preparation (whether formed from slowly freezing liquid or from subliming gas) and independent of attempts to anneal the sample by raising its temperature
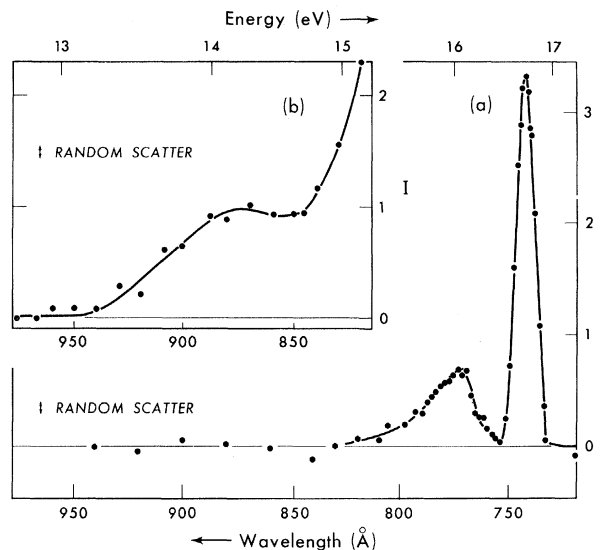

FIG. 1. Luminescence spectrum of solid neon at $T = 14$°K (vapor pressure $<5 \times 10^{-3}$ Torr). The intensity I is in units of 10^3 counts, with photomultiplier-tube dark current subtracted. (a) Data at 12-Å resolution, 1-min sampling time per point. (b) Data at 24-Å resolution, 4-min sampling time per point.

(to within 3°K of the triple point) between spectral measurements. The absolute intensity of the spectral features is reproducible to within a factor of 2 from run to run and from sample to sample. The measured width of the line at 743 Å, limited by instrumental resolution, is unaffected by changing the pressure from 20 to 90 Torr. The intensity of the line decreases by approximately a factor of 2 as the vapor pressure is raised from 1.2 Torr at 16°K to 66 Torr at 21°K.[10]

The spectrum of liquid neon (shown in Fig. 2) is characterized by a main peak located at 774 Å and having a FWHM of about 30 ± 5 Å. The long-wavelength tail of this peak appears to indicate a faint additional structure in the region near 900 Å. The shape of the liquid spectrum is unaffected by changing the liquid depth from 3 to 10 mm. The intensity of the spectrum of liquid neon is considerably smaller than that in the solid (i.e., the intensity of the peak at 774 Å in the liquid is approximately 8 times smaller than the corresponding peak in the solid). The low intensity of the luminescence in the liquid is probably due to the presence of impurities. These appear to affect the liquid more than the solid and may be introduced by the outgassing of the gas-handling system, although the neon used in the measurements is initially very pure.[7]
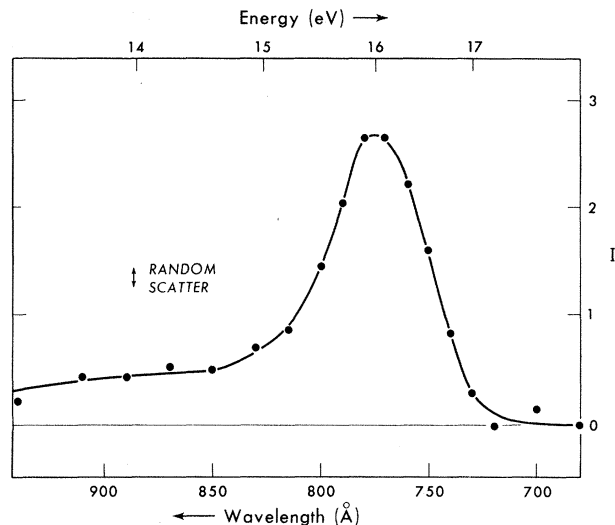
FIG. 2. Luminescence spectrum of liquid neon at $T = 25.4°K$. The intensity I is in units of 10^3 counts, with photomultiplier-tube dark current subtracted. Data taken at 44-Å resolution, 2-min sampling time per point.

The luminescence of neon gas was also briefly examined at several different temperatures. At $T = 55°K$, the spectrum at low densities ($P < 40$ Torr) consists of a single narrow line near 743 Å. At higher densities ($P > 100$ Torr) this line broadens to longer wavelengths and a second broader line appears near 800 Å. As the pressure is increased, this second line grows in intensity while the intensity of the line near 743 Å decreases. At lower temperatures (near $T = 25°K$) and comparable densities the narrow line near 743 Å persists, but the line at 800 Å does not appear.

To complement our measurements on solid neon, it seemed of interest to examine another rare-gas solid at low temperatures. Our measurements on solid argon at 14°K show no narrow line comparable with that in solid neon, but only the spectrum previously reported[1] at 77°K by α-particle excitation, namely, a single broad peak at 1267 Å (with a FWHM = 80 Å).

Before discussing the emission spectra of solid and liquid neon, it is useful to recall the salient features of the known emission spectra of the other rare-gas elements. Studies have been made of solid and liquid argon, krypton, and xenon,[1] as well as of liquid helium.[4,5] Each of these systems has an emission spectrum which exhibits one or two broad lines in the v-uv region. In each case the positions of the lines in the solid and liquid phases agree closely with those ob-

served in the electrical discharge spectrum of the corresponding gas.[11] (The positions, except for liquid krypton, agree within about 3%. The widths agree to within about 20%.) These spectral features have been attributed to transitions of the respective diatomic rare-gas molecules.

Turning now to our data on the emission spectrum of neon, we note first the existence in the solid of broad lines at 774 and 890 Å. The first of these lines appears also in the liquid, and there are indications that the second line appears there too. The appreciable widths of these lines, as well as their presence in both the solid and liquid phases, suggest that these lines are due to transitions of the Ne_2 molecule. It is, however, noteworthy that unlike the case of the other rare gases, the positions of these lines do not correspond to those observed in the discharge spectrum of neon gas.[12]

The most striking feature of the emission spectrum of solid neon is the narrow line, at 743 Å, which does not appear in liquid neon and which corresponds closely to the lowest-frequency transition (at 743.7 Å) observed in the Ne atomic spectrum. This line has no analog in the known spectra of the other rare-gas solids or liquids. Its small width (FWHM < 3.6 Å) suggests that this line is not of molecular origin. Both the absolute intensity of this line, and its intensity relative to the other lines in the emission spectrum, are reproducible between different samples; are not functions of time; and are insensitive to different methods of sample preparation (sublimation of the gas or freezing of the liquid). These experimental results lead to the respective conclusions that the line is due neither to impurities, nor to defects produced by the β source, nor to lattice defects.[13] The data thus suggest that the narrow line at 743 Å is a nonmolecular excitation (i.e., an exciton) characteristic of solid neon.

These results lead us to inquire why the emission spectra of neon are significantly different from those observed in the other rare-gas solids and liquids. After being produced by electron bombardment, the excited states of these other substances do not live long enough to radiate light before they decay to form electronically excited diatomic rare-gas molecules. Radiation from these molecules then gives rise to the observed emission spectra. Our data on neon gas do indeed suggest that the time τ_f required to form a Ne_2 molecule may be long at low temperatures. To be specific, the broad line at 800 Å,

present in the dense gas and presumably of molecular origin, disappears as the temperature is reduced (so that only the narrow line near 743 Å, of atomic origin, remains). A long time τ_f in solid neon at the low temperatures of the experiments would result in the survival of an atomic-like excited state, in the absence of excessive decay due to Ne_2 formation, and could thus be responsible for the observed narrow line at 743 Å. The high degree of order of the solid might also favor the survival of this line (as opposed to the situation in the liquid), as might quantum effects due to zero-point vibration in this very light solid.

It is likely that the thermalizing time τ_t, required by a diatomic rare-gas molecule to decay to its lowest vibrational state, might also be much longer in the case of neon. Compared with the heavier rare gases, the vibration frequency of the diatomic molecule is much larger than the maximum lattice vibration frequency (corresponding to the Debye temperature Θ_D).[14] Under these circumstances and at temperatures less than Θ_D, thermalization of the vibrationally excited molecule by interaction with phonons might be a rather slow process.[15] The molecular-emission spectrum in solid neon at low temperatures might thus be very different from that observed in gas discharges.[16]

If the narrow line at 743 Å does indeed indicate the existence of an atomic-like exciton state in solid neon, it still remains to be explained why this line is so close to the transition in the free Ne atom. It would also be of interest to inquire whether a similar narrow line would also be observed in the other light rare-gas solid, namely solid helium, although (as pointed out previously) an actual experimental observation seems precluded by experimental difficulties. Finally, it is worth noting that Basov et al.[17] have suggested the use of rare-gas solids, pumped by electron beams, to produce lasers at ultraviolet frequencies. The narrow line in solid neon might make this transition a potential candidate for such laser applications.

[1]For work on emission spectra and for further references, see J. Jortner, L. Meyer, S. A. Rice, and E. G. Wilson, J. Chem. Phys. 42, 4250 (1965).

[2]For work on absorption spectra and for further references, see G. Baldini, Phys. Rev. 137, A508 (1965); also B. Raz and J. Jortner, Proc. Roy. Soc., Ser. A 317, 113 (1970).

[3]C. M. Surko, G. J. Dick, F. Reif, and W. C. Walker, Phys. Rev. Lett. 23, 842 (1969).

[4]C. M. Surko, R. E. Packard, G. J. Dick, and F. Reif, Phys. Rev. Lett. 24, 657 (1970).

[5]M. Stockton, J. W. Keto, and W. A. Fitzsimmons, Phys. Rev. Lett. 24, 654 (1970).

[6]The monochromator used was a McPherson model No. 235, equipped with a 1200 line/mm platinum-coated reflection grating blazed at 700 Å.

[7]Mass-spectrometric analysis of the gas shows less than 4 ppm of any one impurity.

[8]In neon gas at 77°K we detected, near 1215 Å, a weak and unreproducible signal which disappeared at lower temperatures. We believe that this signal was caused by impurities, perhaps by hydrogen. In solid neon we have no evidence of an emission peak at 1235 Å, previously reported in Ref. 1.

[9]All line-width determinations were based on measurements with higher resolution than those shown in the figures. Resolution less than 3.6 Å was, however, not practical without inordinately long counting times.

[10]It is probable that the observed intensity decrease is due to absorption in the vapor at the higher pressures, although a direct temperature dependence of the line in the solid cannot be ruled out.

[11]See data on "condensed discharges" in R. E. Huffman, J. C. Larrabee, and Y. Tanaka, Appl. Optics 4, 1581 (1965).

[12]The gaseous-neon discharge spectrum [Y. Tanaka, A. S. Jursa, and F. J. LeBlanc, J. Opt. Soc. Amer. 48, 304 (1958)] shows an edge at 743 Å broadened to longer wavelengths (FWHM ≈ 50 Å) and a broad peak at 830 Å (FWHM ≈ 80 Å).

[13]A narrow emission line excited by x rays in solid krypton has been observed, but its time dependence indicates that it is due to defects induced by the x rays. [M. Creuzburg and K. Teegarden, Phys. Rev. Lett. 20, 593 (1968).

[14]Parameters describing the rare-gas molecules may be estimated by arguments similar to those used for Xe_2 by R. S. Mulliken [J. Chem. Phys. 52, 5170 (1970)].

[15]Very long vibrational relaxation times have been observed at low temperatures for impurity molecules in solid rare-gas hosts. [See D. S. Tinti and G. W. Robinson, J. Chem. Phys. 49, 3229 (1968).]

[16]The electronically excited diatomic molecule is likely to be formed in highly excited vibrational states since the equilibrium internuclear separation of the molecule is significantly smaller than the internuclear

separation in the solid or liquid (see Ref. 14). The observed transitions at 774 and 890 Å might then correspond to transitions from near the classical "turning points" of these highly excited vibrational states.

[17]N. G. Basov et al., Pis'ma Zh. Eksp. Theor. Fiz. 7, 404 (1968) [JETP Lett. 7, 317 (1968)].

Thermal Expansivity and Ultrasonic Propagation Near the Structural Transition of SrTiO₃

Brage Golding

Bell Laboratories, Murray Hill, New Jersey 07974

The thermal expansivity and ultrasonic response of SrTiO₃ have been studied in the vicinity of its structural transition. The nature of the expansivity discontinuity indicates that the transition is second order and that the temperature region in which critical fluctuations are appreciable is less than the strain-broadened transition width. The ultrasonic behavior near T_a is complex and appears to be dominated by structural inhomogeneities.

Although the physical properties of SrTiO₃ have been nearly exhaustively characterized there exists little detailed information about their behavior near the structural transition temperature T_a.[1-9] We have performed high-resolution, <u>simultaneous</u> measurements of thermal expansivity and ultrasonic propagation near T_a for single crystal SrTiO₃. We find that the SrTiO₃ transition is second order in the Ehrenfest classification and that the temperature region in which critical fluctuations are appreciable is less than the strain-broadened transition width, $\Delta T/T_a \simeq 5 \times 10^{-4}$. The spontaneous volume strain below T_a is large and is consistent with recent measurements of the pressure dependence of T_a. The transition temperature is sample dependent and differs by 0.53 K for two specimens investigated. From the location of T_a obtained from the expansivity discontinuity, it is possible to unambiguously establish the behavior of the sound velocity and attenuation relative to the transition. In contrast to previous work,[10] the data are not consistent with the existence of a singular contribution to the elastic constants above T_a. Below T_a, our ultrasonic results at 10^7 Hz show complex behavior and cannot be derived from a relaxation analysis of high-frequency (~2 ×10¹⁰ Hz) Brillouin scattering measurements.[11] Finally, we point out that very small inhomogeneous strains present in Verneuil-grown SrTiO₃ can make spurious contributions to ultrasonic attenuation near T_a. The effect would be reproducible, though sample dependent, and could explain discrepancies which exist among several previous ultrasonic investigations.[12-15]

Linear expansivity was measured in ⟨110⟩ and ⟨111⟩ directions by means of a high-sensitivity three-terminal capacitance technique capable of detecting thermal strain ~10^{-9}. Ultrasonic velocity changes were measured simultaneously on the ⟨110⟩ crystal in orthogonal ⟨001⟩ or ⟨1$\bar{1}$0⟩ directions using a frequency-modulated pulse superposition method with sensitivity ~10^{-7}. To assure thermal homogeneity, the copper expansion cell containing the sample was suspended by fine wires inside a sealed copper can and heated indirectly through exchange gas. Thermal isolation of the inner can from the surrounding liquid-nitrogen bath was achieved by an outer can in which a high vacuum was maintained. The details of the experimental apparatus and techniques will be described elsewhere. Temperature was measured with a platinum thermometer operated in an ac bridge circuit. All data were taken after the establishment of thermal equilibrium as indicated by stability of thermometer ($\Delta T \simeq \pm 10^{-4}$ K), velocity, and capacitance readings.

Thermal strain in the transition region for two different SrTiO₃ crystals and orientations is shown in Fig. 1. A discontinuous change in slope occurs at a temperature which we identify as the structural transition temperature for that sample. For the ⟨111⟩ oriented crystal, T_a is 105.86 ± 0.07 K whereas for the ⟨110⟩ sample it is 105.33 ± 0.07 K.[16] The linear thermal expansivity discontinuity along ⟨111⟩, $\Delta\alpha_L^{\langle 111\rangle}$, is independent of the structural domain distribution which exists below T_a and we have

$$\Delta\alpha_L^{\langle 111\rangle} \equiv \frac{1}{l}\frac{dl}{dT}\bigg|_{T=T_a^+} - \frac{1}{l}\frac{dl}{dT}\bigg|_{T=T_a^-} = \tfrac{1}{3}\Delta\alpha_V, \quad (1)$$

where $\Delta\alpha_V$ is the isobaric volume expansivity discontinuity. A linear least-squares fit to the