

we compute a thermodynamic critical field of 57 Oe. Assuming a parabolic critical field curve, we compute from this an electronic specific heat, γ , equal to $0.050 \text{ mJ/cm}^3 \text{ }^\circ\text{K}^2$. Though this value is close to that for metallic silver ($0.065 \text{ mJ/cm}^3 \text{ }^\circ\text{K}^2$), it is clear that the conduction bands must be much narrower and the effective masses much larger in the clathrate than in metallic silver, since the electron density is undoubtedly much lower in the clathrate.

The fact that the superconducting transition temperature of the nitrate salt is three to six times as high as those of the fluoride and fluoroborate salts suggests that isotope effect experiments might give useful information. Such

experiments are under way.

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RELATIVE QUANTUM YIELD FOR PHOTOEMISSION FROM THIN FILMS OF XENON AND KRYPTON

J. F. O'Brien and K. J. Teegarden*

Institute of Optics, University of Rochester, Rochester, New York

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The photoelectric yield for thin films of xenon and krypton has been studied from 7.5 to 11.7 eV. For solid xenon a direct emission threshold is observed at 9.7 eV, and the electron affinity is estimated to be 0.39 eV. No threshold occurs in krypton below 11.7 eV, but emission associated with defect centers is observed below threshold in both materials. Measurement of the energy distribution of the emitted electrons could not be made because of strong polarization effects produced by the electron emission.

The experimental equipment has been described elsewhere.^{1,2} The cryostat was isolated from the monochromator by a lithium fluoride win-

dow and pumped to a base pressure of 5×10^{-9} Torr by a Vac-Ion pump. The samples were deposited on substrates at 20°K, and film thicknesses of several hundred angstroms were estimated from comparison with the absorption data taken by Baldini,³ shown in Fig. 1. Since the films were polarized by the emission of electrons, all data were taken at low light intensities and at voltages far above the saturation level.

Figure 2 is a curve of the quantum yield, in

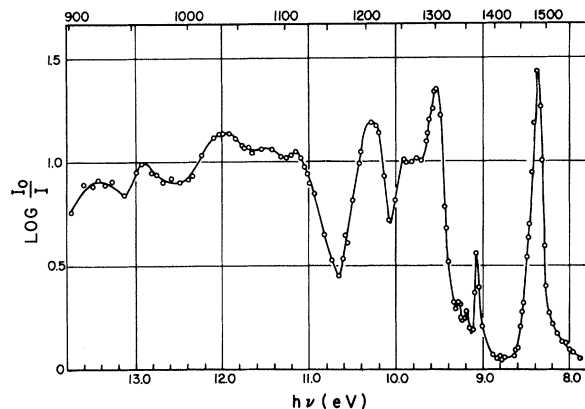


FIG. 1. Absorption spectrum of solid Xe at 12°K (annealed at 53°K), after Baldini.³

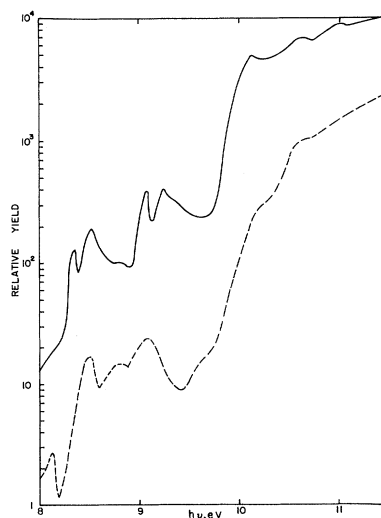


FIG. 2. Relative quantum yield in arbitrary units of solid Xe at 20°K on a Pt substrate. Unannealed film (dashed). Film annealed at 55°K (solid).

arbitrary units, for emission above the saturation voltage from a xenon film on a platinum substrate at 20°K. For clarity, the curves for the annealed and unannealed film have been shifted vertically. Onset of direct optical transitions to conduction-band states above the vacuum level is indicated by the sharp threshold near 9.7 eV, where the yield rises to about 10% at 11.7 eV. The structure observed below threshold is similar to emission from alkali halides containing color centers.⁴ Since the final state of the optical transition is below the vacuum level in this region of the spectrum, the emission is assumed to occur after interaction of the excited state of the crystal with a defect center. The nature of the defect centers is not known and no impurities have been optically observed in the films.

The emission peak at 8.5 eV and the shoulder at 9.6 eV in the unannealed film coincide with the Frenkel exciton transitions $\Gamma_8^- \rightarrow \Gamma_6^+$ and $\Gamma_6^- \rightarrow \Gamma_6^+$. Upon annealing, the $\Gamma_6^- \rightarrow \Gamma_6^+$ transition is obscured by the threshold and the $\Gamma_8^- \rightarrow \Gamma_6^+$ transition is red-shifted to 8.4 eV. The dip at 8.4 eV is a surface effect caused by the large absorption coefficient ($>10^6 \text{ cm}^{-1}$) in the center of the absorption peak, and the same effect has been observed in alkali halides.⁴ Reflectivity, which is not included in the calculation of the yield, may also be partly responsible for the dip.

In the unannealed film, the Wannier exciton series³ is seen only as a broad band at 9.1 eV, but the $n=2$ line appears at 9.07 eV in the annealed film. The remaining lines of the series and the ionization edge produce a broad emission band at 9.3 eV. Peaks occurring at 8.15 and 8.8 eV in the unannealed film are due to emission from the substrate and are not observed when a lithium fluoride substrate is used.

For several data runs on annealed films, the threshold from 9.7 to 10.1 eV has been fit by a quadratic, $Y=C(E-E_T)^2$. Analysis indicates a threshold energy $E_T=9.7 \pm 0.02$ eV. Using the recently calculated band structure of xenon,⁵ the vacuum level is placed at 9.67 eV above the top of the valence band at Γ_8^- , and the electron affinity is calculated to be 0.39 eV for a band gap of 9.28 eV.³

A consistent feature in the data above the threshold is the sharp dip centered at 10.3 eV. This is attributed to the exciton line observed in the absorption spectrum at this energy. Absorption in the exciton line, which has a low-

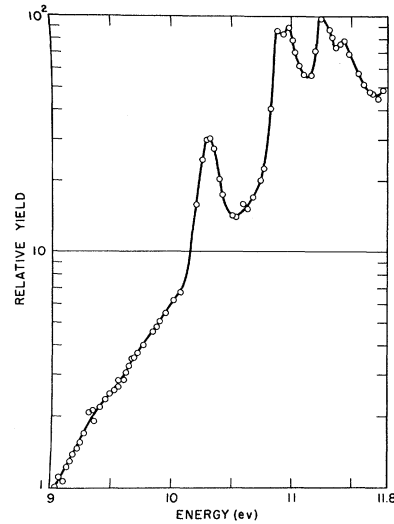


FIG. 3. Relative quantum yield in arbitrary units of solid Kr at 20°K (annealed at 45°K).

er emission yield than a conduction-band state, reduces the number of conduction-band transitions and produces the dip in the yield.

The line at 10.3 eV and the Frenkel exciton lines have been observed in the reflectivity of liquid xenon,⁶ and this fact was used to argue against Phillips's interpretation⁷ of the 10.3-eV line as a hybrid L exciton. We note that a strong absorption line occurs in atomic xenon at 10.4 eV for the $5d[1 \frac{1}{2}]^o$ transition.⁸ A peak might thus be expected near this energy in the liquid. The same line can also be identified in the absorption spectrum of a dilute mixture of xenon in solid argon.⁹ This is a strong argument for an essentially atomic nature of the line. Peaks for the $5p-6s$ transitions are observed at 8.45 and 9.58 eV in the atom. Thus the Frenkel lines and the 10.3-eV line all appear at the same energy, within 0.1 eV, in the solid, liquid, and gas phases of xenon. The line strengths in the solid have roughly the same ratio as in the gas, if an absorption background due to conduction-band states is subtracted. This suggests that the 10.3-eV line is a Frenkel exciton state with the electron in a $5d$ atomic state. A weaker $5d[0 \frac{1}{2}]^o$ transition occurs in the atom at 9.95 eV and may account for some of the structure observed in the solid between 9.6 and 9.9 eV.

Shown in Fig. 3 is the relative quantum yield for an annealed krypton film. The Frenkel exciton lines are observed at 10.3 and 10.9 eV, and the $n=2$ Wannier line at 11.24 eV is resolved from the rest of the Wannier series. The yield is less than 0.5%, and no threshold is observed

below the lithium fluoride cutoff at 11.7 eV.

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NEW ELECTRON-TUNNELING MEASUREMENT OF THE ENERGY GAP IN LANTHANUM

J. J. Hauser

Bell Telephone Laboratories, Murray Hill, New Jersey

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Edelstein and Toxen¹ recently reported electron-tunneling measurements of the energy gap of lanthanum with the result that $2\Delta_0/kT_c = 1.65$. On the other hand, using similar measurements, we have found a value of 3.2 for $2\Delta_0/kT_c$, which is in much closer agreement with the BCS theoretical value of 3.52. It is possible that the difference between these experimental results is due to a large extent to the method of preparation of the lanthanum films.

The tunnel diodes were prepared by evaporating a 0.25-mm-wide strip of aluminum approximately 1000 Å thick onto a sapphire substrate, oxidizing it, and depositing a cross strip 0.25 mm wide of lanthanum by getter evaporation. The getter-evaporation technique was very similar to the getter-sputtering technique previously described.² This technique consists in evaporating the lanthanum with a mask over the substrate inside a small liquid-nitrogen-cooled can, so as to getter the interstitial gases such as oxygen and nitrogen. Subsequent-

ly, the mask is removed and the film is deposited in a much purer atmosphere than that of the bell jar (in the 10^{-6} -mm range). As lanthanum is very easily contaminated, the best results were obtained by keeping the substrate table at 77°K and keeping the junction under liquid nitrogen until measured. Since the tungsten filament from which the lanthanum was evaporated was at 2000°C and approximately 3 cm from the table, the substrate temperature was undoubtedly much above 77°K.

As can be seen from Table I, this technique yields films which when thick enough ($\approx 10\,000$ Å) have an appreciably better resistance ratio than those reported previously.¹ The higher resistance ratio of the films evaporated at higher temperatures is most probably due to grain growth. A further difference between the films described by Edelstein and Toxen¹ and those described in Table I is the higher transition temperature of the latter. This higher transition temperature (as high as 6.7°K) seems to

Table I. Physical properties of lanthanum films.

Sample	T_c (°K)	ρ (room temperature)/ ρ (7°K)	Thickness (Å)	Temperature of substrate table (°K)
La-1	6.65	7.2	4775	77
La-3	6.2	8	10 000	300
La-5	6.35	14	18 450	900
La-6	6.74	16	8000	700
La-8	5.24	•••	2680	77
Al-Al ₂ O ₃ -La No. 2	5.00	4	2500	77
Al-Al ₂ O ₃ -La No. 3	5.15	3.8	2000	77
Al-Al ₂ O ₃ -La No. 7	5.26	6.8	4000	77
Al-Al ₂ O ₃ -La No. 9	5.85	8.1	10 500	77