

Effects of pressure and temperature on the optical absorption spectrum of lead azide

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Optical absorption spectra of lead azide (PbN_6) have been obtained at room temperature for pressures up to 22 kbar and at 1 bar for temperatures down to 77 K. The shift of the 3.35 eV absorption peak is discussed in terms of various exciton models.

I. INTRODUCTION

Studies of the optical properties of lead azide thin films by several investigators have generated a variety of interpretations of the structure observed in the optical absorption spectrum. The models proposed include effective mass,¹ Frenkel tight-binding, and charge-transfer type excitons.¹⁻³ For the tight-binding type, both intracation and intraanion transitions have been proposed. We present here measurements of the effect of hydrostatic pressure and temperature changes on the edge and the long wavelength peak in the absorption spectrum. It is hoped that this information may lead to a better understanding of the band structure and exciton behavior in lead azide.

II. EXPERIMENTAL

A Wier-Van Valkenburg type cell was used for the pressure measurements.⁴ Basically, it consists of a hydrostatic medium within a gasketed region between two opposed diamond anvils to which an axial force is applied. Pressure calibration derives from the observation of the melting point of the medium. Lead azide films were grown on one anvil face using previously described techniques.¹ A 300 Å film of metallic lead was vacuum evaporated onto the diamond and then allowed to react with gaseous hydrazoic acid (HN_3). The final film thickness is thus about 1000 Å. A gasket of Inconel steel was then placed over the film and flooded with the hydrostatic fluid (e.g., hexane, m.p. = 10.4 kbar, ethanol, m.p. = 22.2 kbar, at room temperature⁵). The cell was then assembled and sufficient force was applied to seal the fluid and to cause it to crystallize. At this point, the force was carefully reduced until the fluid medium melted. The use of the melting point rather than the freezing point avoids the problem of the medium "superpressing" to abnormally high pressures. The pressure cell was rigidly fixed in the sample compartment of a Cary 14-R spectrophotometer so that the pressure could be released without moving the film with respect to the beam. Spectra were obtained through the diamonds, fluid and film as well as through the diamonds and fluid alone in order to make the appropriate corrections. Temperature coefficients of the absorption edge and exciton peaks were obtained from films reacted on sapphire substrates and mounted in a gas exchange dewar which provided accurately controlled temperatures.

III. RESULTS AND DISCUSSION

Typical spectra obtained after subtraction of the background due to the diamonds and the pressure medium are shown in Fig. 1. Since the diamond absorption interferes considerably with the determination of the azide spectra at higher energies, the curves are arbitrarily normalized at 2.2 and 3.6 eV. This allows one to obtain the shift in the exciton peak position as a function of pressure, but makes it difficult to determine the shift of the absorption edge in a quantitative manner.

It is apparent, however, that the exciton peak position in lead azide shifts to lower energy and away from the band edge as pressure is increased. The pressure coefficient at room temperature between 1 bar and 22 kbar is $(-4 \pm 1.5) \times 10^{-6}$ eV/bar. The temperature coefficient at 1 bar for the peak position between room temperature and 77 K was found to be $(-1.4 \pm 0.3) \times 10^{-4}$ eV/K. The peak sharpened significantly upon cooling the film, and similar sharpening can be seen in the pressure data.

Several interpretations of the low energy exciton peak in the spectrum of lead azide have been considered including intraanionic and intracationic excitons, charge transfer excitons and effective mass or Wannier excitons.¹⁻³ A further alternative, suggested by Deb,⁶ incorporates the idea of three distinct valence bands¹ but with the transitions occurring between these bands and a discrete level lying slightly below the bottom of the conduction band. Detailed band structure calculations have not been performed for lead azide due to complications arising from the existence of two distinct types of

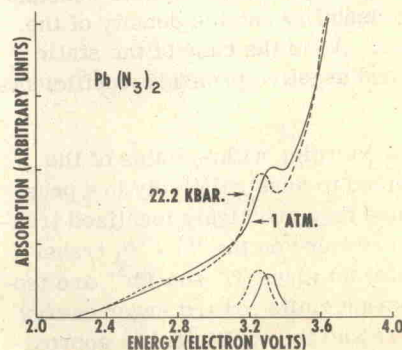


FIG. 1. Optical absorption spectra of lead azide at 1 and 22.2 kbar.

Pb^{2+} sites and four types of N_3^- , however, Madelung energy calculations have been made and the energy of charge transfer excitons estimated as 3 to 4 eV from the von Hippel cycle.⁷

Different effects are expected for the various types of excitons under the influence of pressure. Pressure coefficients for charge transfer excitons should be positive provided that the change in polarization energy remains small, even taking into account the nonisotropic compressibility of lead azide.⁸ The principle energy dependence then goes as R^{-1} , where R is the cation-anion separation. The effect of pressure is to decrease this distance and thereby to increase the transition energy.

Effective-mass type excitons, referred to the top of the valence band, have energies approximated by⁹

$$E_n = E_g - \mu e^4 / 2 \hbar^2 \kappa^2 n^2, \quad (1)$$

where μ represents the reduced effective mass, κ the appropriate dielectric constant, n the principle quantum number, and e the electronic charge. Both band broadening and a shift of energy bands can be induced by pressure. The effect of pressure on the band gap of lead azide is uncertain from our data, however, our work does show that the exciton transition shifts away from the band edge. Thus, the second term on the right of Eq. (1) must increase with increasing pressure. Since the density of states decreases due to band broadening, the effective masses (and therefore the reduced effective mass) decrease also. The choice of the appropriate dielectric constant depends on the spatial extent of the exciton and may be the static or optical or some average of the two.⁹ In order for the effective-mass exciton model to be consistent with the data the appropriate dielectric constant must decrease with increasing pressure, at a rate which exceeds the rate of decrease of the reduced effective mass.

The effects of temperature and pressure on the dielectric constants of PbN_6 are not known. Several factors influence the pressure dependence of the static constant including the infrared resonance frequency and the ionic charge as well as the contribution from the optical constant.¹⁰ Values of pressure derivatives of the static constant have been determined for a large number of dielectrics and both positive and negative values are observed.^{11,12} Among the factors which determine the pressure dependence of the optical constant are the electronic polarizability and the density of the polarizable constituents. As in the case of the static constant both positive and negative pressure coefficients have been observed.¹³

Intracation transition energies within states of the Pb^{2+} ion would be expected to have relatively low pressure coefficients because they are highly localized transitions. The effect of pressure on the $^1S_0 - ^1P_1$ transition of Ti^+ in KCl is relevant since Ti^+ and Pb^{2+} are iso-electronic. This transition shifts toward lower energy with increasing pressure and the coefficient is approxi-

mately the same as that observed for the exciton transition in PbN_6 .¹⁴ This analogy must be viewed cautiously since the local symmetry of the Ti^+ in KCl is considerably different from that of Pb^{2+} in lead azide, and we have completely ignored admixture of valence band states. However, it may serve to indicate that a shift toward lower energy with pressure is not inconsistent with the intracation exciton model.

The temperature shift, measured between 77 and 300 K, may be analyzed using the relationship

$$\left[\frac{\partial E}{\partial T} \right]_P = \left[\frac{\partial E}{\partial T} \right]_V - \frac{\alpha}{\beta} \left[\frac{\partial E}{\partial P} \right]_T, \quad (2)$$

in which E is the transition energy, α the volume isothermal expansion coefficient, and β the isothermal compressibility. Assuming $\alpha = 9.86 \times 10^{-5}/\text{K}^{15}$ and $\beta = 2.44 \times 10^{-6}/\text{bar}$,⁵ the value obtained for $(\partial E/\partial T)_V$ is -3.02×10^{-4} eV/bar, a relatively large figure which indicates that the observed temperature shift of the exciton peak is influenced considerably by the electron-phonon interaction.

In summary, the observed shift of the exciton peak toward lower energy with increasing pressure argues against the charge transfer model, while leaving the effective-mass type and intraionic excitons as viable descriptions. If the exciton is indeed the effective-mass type then the dielectric constant appearing in Eq. (1) decreases with increasing pressure.

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