ELECTRON ENERGY LOSS MEASUREMENTS ON PbF_2, $PbCl_2$, $PbBr_2$ AND PbI_2

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The results of electron energy loss measurements on polycrystalline films of PbF_2, $PbCl_2$, $PbBr_2$ and PbI_2 are presented, and the calculated dielectric functions are discussed in relation to their band structures and optical data.

The lead halides are ionic materials with different crystal structures. PbI_2 is an anisotropic semiconductor which crystallizes in the layered structure of CdI_2 (2H polytype) and also in the $CdCl_2$ structure. When prepared by evaporation, PbI_2 forms layers with the c-axis perpendicular to the surface of the film. $PbCl_2$ and $PbBr_2$ crystallize in the $PbCl_2$ structure [1], while PbF_2 has two phases, cubic (fluorite) and orthorhombic [2], the latter being the most stable phase below 250°C. Their fundamental absorption edge spectra are characterized by various sharp excitonic peaks [3–5] which seem to originate from cationic 6s → 6p transitions on the lead ion, rather than from transitions from the nonmetal to the metal ion states characteristic of the alkali halides [4].

The band structure and optical properties of PbI_2 have been studied by various authors [4–9]. Beaumont et al. [4] report on the optical constants of PbI_2 and PbF_2 between the fundamental absorption and 130 eV deduced from their reflectivity and transmission measurements using synchrotron radiation. They observe several sharp peaks between 18 and 25 eV and assign them to the 5d → 6p transitions on the Pb^{2+} ion which they discuss as core excitons. Similar structures were observed by Buchner [10] in the energy loss spectra of the lead chalcogenides, showing no energetic shift for all $\boldsymbol{k}$-transfers, and assigned them to band transitions at Γ from flat valence bands. Amitin et al. [3] discuss the electronic structure of $PbCl_2$ on the basis of reflectivity measurements in the 2–10 eV region. Optical data on PbF_2, $PbCl_2$ and $PbBr_2$ are scarce, and there are no band structure calculations for these.

This work was done with the purpose of presenting the small scattering angle energy loss spectra of the lead halides in the spectral region from the fundamental absorption to 50 eV, which includes the interband transitions and the first core excitations, and to report the calculated dielectric functions of these compounds as a means of comparing and discussing their electronic structures.

The experiments were performed with 45 keV electrons in a transmission energy loss spectrometer [11] modified for high resolution measurements [12]. The energy resolution was between 0.1 eV and 0.3 eV, the poorer value corresponding to the highest scattering angle measurements. The scattering angle (wavevector) resolution was 0.15 mrad (0.016 Å^{-1}). The samples, prepared by vacuum evaporation onto formvar (polyvinyl formal) substrates were polycrystalline films with estimated thicknesses of about 500 Å. Room temperature energy loss spectra were recorded in the energy range 0–50 eV for various scattering angles up to 1 mrad, corresponding to momentum transfers of up to 0.11 Å^{-1}.

It is known that in a single scattering event, the probability that a fast electron moving through a solid transfers momentum $\hbar\boldsymbol{k}$ and energy $\hbar\omega$ to it is given by:

$$P(\boldsymbol{k}, \omega) = C\,k^{-2}\,\mathrm{Im}\{-1/\epsilon(\boldsymbol{k}, \omega)\}\,, \qquad (1)$$

where $\boldsymbol{k}$ is the wavevector, $\epsilon(\boldsymbol{k}, \omega) = \epsilon_1(\boldsymbol{k}, \omega) + \mathrm{i}\epsilon_2(\boldsymbol{k},$

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ω) is the dielectric function, and C is a constant which includes experimental parameters such as the sample thickness [14,15]. The measured probability may also include contributions from inelastic processes such as Čerenkov radiation or surface losses, but these can be neglected when the spectra are recorded at non-zero scattering angles. The contribution from electrons that undergo multiple inelastic losses was minimized by choosing sample widths of the order of the mean free path for volume excitations. The real and imaginary parts of the dielectric function were calculated through the corresponding Kramers–Kronig relation: the function $\mathrm{Re}\{1/\epsilon(k, \omega)\}$ is calculated from the experimental $\mathrm{Im}\{-1/\epsilon(k, \omega)\}$, and then the dielectric function is evaluated after scaling the result. The scaling was done through known optically determined values of $\epsilon(k = 0, \omega)$. Since the samples studied here are semiconductors or insulators, it was found convenient to scale the results to known values of the refractive index $n = \sqrt{\epsilon_1}$ measured at frequencies below the band gap where $\epsilon_2 = 0$. Once the dielectric function is known, the optical constants may be deduced for comparison with optical data. A useful quantity that can be derived from ϵ_2 is the effective number of electrons

$$n_{\mathrm{eff}}(\omega) = \int_0^{\omega} J(\Omega)\,\mathrm{d}\Omega = \frac{m}{2\pi^2 e^2 N} \int_0^{\omega} \Omega \epsilon_2(\Omega)\,\mathrm{d}\Omega, \quad (2)$$

where e and m are the electron charge and mass, N is the number of unit cells per unit volume, and J is the optical joint density of states which has units of states per unit cell per unit frequency [16]. The integral $J(\omega)$, $n_{\mathrm{eff}}(\omega)$, represents the effective number of valence electrons that contribute to the electronic excitations as a function of the upper integration limit ω.

Energy loss traces of the lead halides are presented in figs. 1 and 2. Fig. 1 shows the $k \approx 0$ (zero scattering angle) spectra, and fig. 2 the normalized energy loss functions corresponding to $k = 0.08$ Å^{-1} measurements. The first low energy peaks in the optical spectra of $\mathrm{PbI_2}$ have been assigned to excitonic transitions at the A point of the Brillouin zone for $\mathrm{Pb^{2+}}$ 6s-like to 6p-like levels, followed by the onset of the anionic gap ($\mathrm{I^-}$ 5p to $\mathrm{Pb^{2+}}$ 6s-like) [4,5]. This is in agreement with our results which show that the intensity of these excitonic peaks, appearing very strong in fig. 1, decreases considerably in the non-zero momentum transfer results of fig. 2, while the peaks associated with the anionic gap at 9.5, 9.2, 7.4, and 6.3 eV in the $k \approx 0$ spectra of $\mathrm{PbF_2}$, $\mathrm{PbCl_2}$, $\mathrm{PbBr_2}$, and $\mathrm{PbI_2}$ remain strong and shift to 10.0, 9.3, 8.4, and 6.8 eV, respectively, for the $k \approx 0.08$ Å^{-1} results. The broad structures observed between 13 and 20 eV in all compounds except for $\mathrm{PbF_2}$ are the volume plasmons. The most obvious similarity between the four energy loss traces is the set of high energy peaks that appear between 18 and 25 eV. These are identified as localized core excitations arising from the 5d → 6p transitions of the $\mathrm{Pb^{2+}}$ ion, with energies very close to those of the free ion. Similar structures have been observed in energy loss measurements on PbS, PbSe, and PbTe [10].

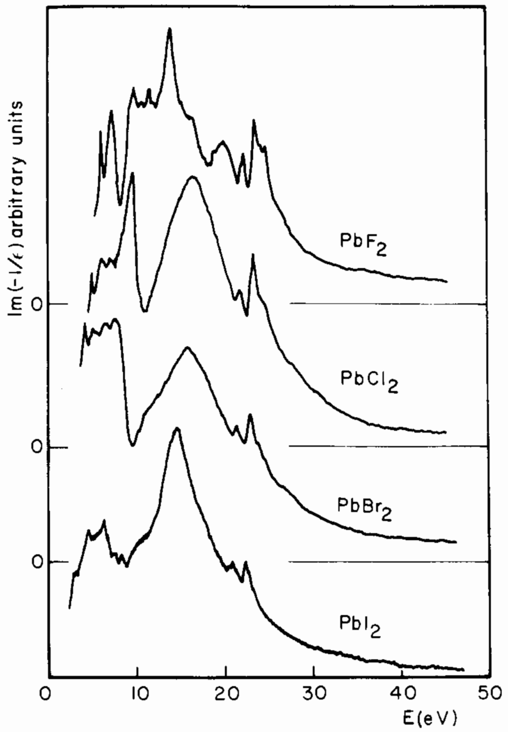

Fig. 1. Energy loss spectra of the lead halides recorded at zero scattering angle.

Fig. 3 shows the dielectric functions $\epsilon(k = 0.08$ Å^{-1}, $\omega)$ of the lead halides obtained by a Kramer–Kronig analysis of the energy loss functions of fig. 2. The accuracy of the measurements and the reliability of the analysis was checked by comparing the absorption coefficient deduced from the dielectric function of $\mathrm{PbF_2}$ with a direct absorption measurement [4]; the result, shown in fig. 4, indicates good agreement,

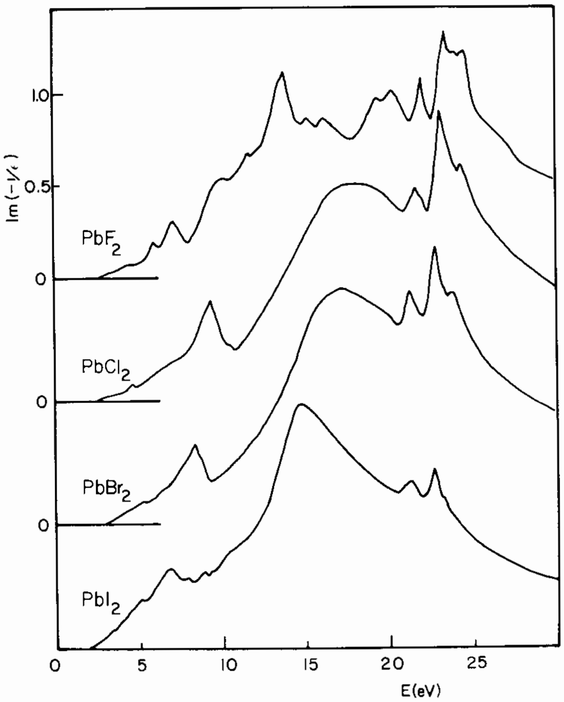

Fig. 2. Energy loss functions of the lead halides from the data recorded at 0.75 mrad corresponding to a momentum transfer of 0.08 Å^{-1}.

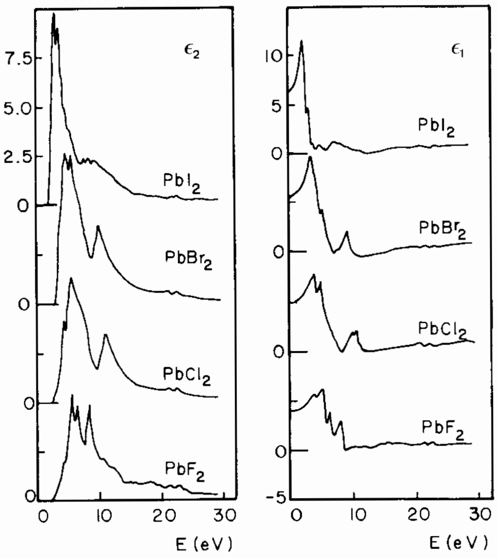

Fig. 3. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of the lead halides calculated from the spectra of fig. 2.

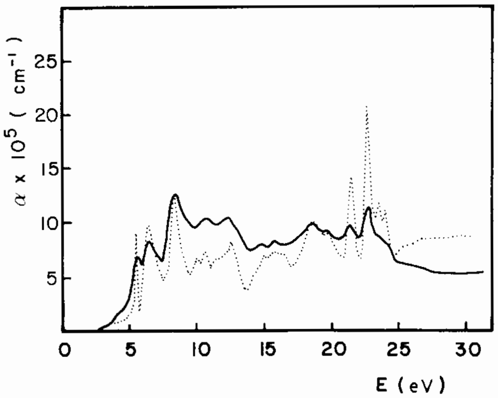

Fig. 4. Absorption coefficient of PbF_2. The full curve was deduced from the corresponding dielectric function of fig. 3. The broken curve was taken from the optical measurements of Beaumont et al. [4].

considering that the synchrotron radiation measurements were done with higher resolution and at low temperature (77 K).

Fig. 5 shows the effective number of electron curves, calculated from the ϵ_2 graphs of fig. 3 using eq. (2). A comparison of the first broad structure in the ϵ_2 spectra indicates a broadening of the valence band with increasing ionicity, from about 2.5 eV in the iodide to 7 eV in the fluoride. The effective number of electrons at the center of this structure in ϵ_2 yields a value of 2, which corresponds to the two electrons/molecule forming the Pb^{2+} 6s-like state at the top of the valence

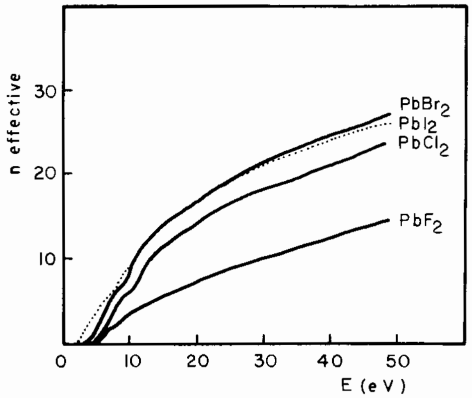

Fig. 5. Effective number of electrons $n_{\mathrm{eff}}(\omega)$ that contribute to the electronic transitions of the lead halides at the energy $\hbar\omega$.

band that contributes to the low energy excitonic transitions associated with the lowest Pb^{2+} 6p-like conduction bands (cationic gap). The following set of transitions in PbI_2, from the I^- 5p-like valence band to the conduction band (anionic gap), leads to a partial saturation of n_{eff} at 6 electrons. This occurs at 7.5 eV, when the six available Pb^{2+} 6p-like conduction band states are filled. A partial saturation at 6 electrons is also observed in $PbBr_2$ and $PbCl_2$ at 8.5 and 10 eV, respectively, indicating that in these compounds, the lowest conduction bands are also 5p-like Pb^{2+} states.

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