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OXYGEN *K* EMISSION SPECTRA OF ICE, SOLID CARBON DIOXIDE, AND SOLID ALCOHOLS*A. S. Koster[†]*Department of Physics, University of Arizona, Tucson, Arizona 85721*

(Received 4 November 1970)

A long-wavelength x-ray spectrometer with a sample holder cooled by liquid nitrogen was used to obtain oxygen *K* spectra from ice, solid CO₂, and solid alcohols. The nature of the peaks is discussed.

Very few soft x-ray emission spectra are known for compounds which are gaseous or liquid at room temperature. Such spectra can be emitted by molecules in the gaseous state or by a solid sample which has been cooled below its melting point. Mattson and Ehlert, using a soft x-ray spectrometer capable of exciting gases, gave oxygen *K* spectra from O₂, CO₂, CO, and N₂O¹ and carbon *K* spectra from a number of carbonaceous gases and vapors; they also indicated the carbon *K* bands from solid CO₂ and benzene.²

The spectrometer used in the present investigation includes a cold cathode x-ray tube, in which the emitting sample is the secondary target; thus cooled, samples remain solid, and a slight evaporation is not harmful since the apparatus is maintained at constant pressure by a controlling device. Details of the equipment have been described in previous publications from this laboratory^{3,4}; for this work the sample holder was modified (a) so that the sample was on top of a small chamber through which coolant (liquid nitrogen) was circulated and (b) to place absorbers in the air inlets of the oil pump and the pressure controller for exclusion of atmospheric water and carbon dioxide. The estimated sample temperature was -160 to -170 °C. A KAP crystal was used for recording the oxygen spectra. The power applied was 7 kV at 10 mA, giving peak intensities of about 50 cps. Figure 1 shows the oxygen *K* bands from ice, carbon dioxide, and methanol. Ethanol, 1-propanol, and 1-butanol, also investigated, yielded a spectrum indistinguishable from that of methanol.

A remarkable aspect of the investigations at liquid-nitrogen temperature was that many organic compounds⁵ decomposed rapidly during excitation, whereas the same or analogous compounds were reasonably stable when emitting at room temperature. This may be due to the extremely small conductivity at -160 °C. For this reason, only thin films of the sample were employed. Among the organic chemical compounds examined only the alcohols were sufficiently stable; others, like ethers, aldehydes, ketones, and heterocyclic compounds, decomposed massively.

The oxygen *K* peak at 532 eV, occurring in all oxygen spectra, is especially prominent when the analyzing crystal is KAP; Liefeld *et al.*⁶ showed

this to be due to enhanced reflectivity. According to Koster⁷ neutral oxygen atoms, created by the impact of electrons or x-ray quanta, cause this peak. The principal peak in the ice and solid methanol spectra occurs at 526 eV. Strongly ionic compounds like MgO and Al₂O₃ show it at 525 eV. The ice spectrum also has a well-defined subpeak at 520 eV; it is due to a transition from one of the molecular orbitals. The main band and also the subpeak are broader in the methanol spectrum; since the methanol molecule has lower symmetry than the water molecule, its number of molecular orbitals is larger.

The ice *K* spectrum checks well with electron spectroscopy data by Siegbahn *et al.*⁸ Using the levels found spectroscopically, we can expect transitions at 507, 520, 523, and 526 eV. Those at 507 and 523 eV, resulting from molecular orbitals with mainly *s* symmetry, have a low probability and are not observed. The transition at 526 eV results from a 1*b*₁ nonbonding orbital (2*p*_z lone pair) and thus could be called an ionic transition; it is a transition of this kind which is most prominent in the mainly ionic oxides.

The oxygen subband at 520 eV stems from a 1*b*₂ bonding orbital (2*p*_x type). It is significant that an analogous band can be detected in the oxygen spectra of even strongly ionic compounds like MgO. Evidently molecular orbitals determine the oxygen

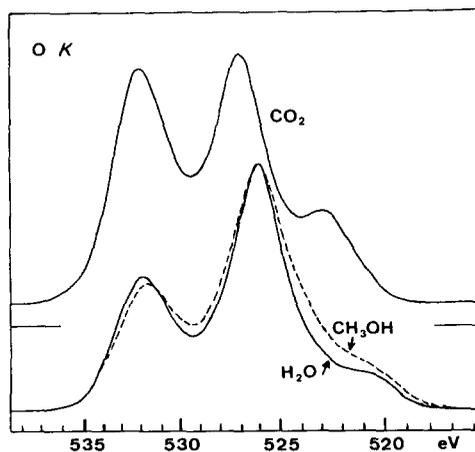


FIG. 1. The oxygen *K* emission band from ice, solidified CO₂, and solidified CH₃OH at about -160 °C. The ordinate is the intensity.

spectra and, for the same reason, the metal spectra. In recent years, the model of crossover transitions has been freely used to explain low-energy satellite lines and line shifts in K spectra of mainly ionic compounds^{7,9}; for instance, $Mg-K_{\beta}$ and $Mg-K_{\beta'}$ in MgO are associated with the $L_{II,III}$ and L_I levels of the O^{2-} ion. Urch's rejection¹⁰ of this model in favor of an entirely molecular orbital model is not to the point, the concepts involved being complementary rather than opposed. The initial level associated with a crossover transition is common to the whole of the crystal, not only to positive or negative atomic sites; it is part of the valence band. The name "crossover transition" depicts more clearly which wave function contributes most.

The oxygen spectrum from solidified CO_2 shows two peaks at 527 and 523 eV. The molecular orbitals connected with these peaks give rise to two peaks in the carbon spectrum of solidified CO_2 .^{2,7} The oxygen K main peak at 527 eV is an "ionic" peak; the corresponding carbon K peak at 283.5 eV is small. The molecular orbital oxygen K peak at 523 eV is related to the main carbon K peak at 279.5 eV. The difference between the $C(1s)$ and $O(1s)$ binding energy thus is 243.5 eV; if we assume the $O(1s)$ binding energy to be 534 eV,⁷ then the $C(1s)$ binding energy is 290.5 eV, in good agreement with electron spectroscopy measurements.¹¹

*This investigation has been carried out in the labora-

tory of Professor Ralph W.G. Wyckoff, supported by a grant from the National Aeronautics and Space Administration to him.

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HOT-PRESSED $CdCr_2S_4$: AN EFFICIENT MAGNETO-OPTIC MATERIAL

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The ferromagnetic semiconductor $CdCr_2S_4$ has been prepared in the form of hot-pressed polycrystalline samples having high optical transmission and Faraday rotation in the near-ir spectral region. In the region 900–1400 nm, the figure of merit exceeds $60^\circ dB^{-1}$ at 4.2°K and $30^\circ dB^{-1}$ at 80°K. It is thus an efficient and potentially useful magneto-optic material at liquid-nitrogen temperature.

A general discussion of the potential uses of Faraday rotation in magnetic crystals has been given by Dillon.¹ In this note, we wish to point out some desirable characteristics of hot-pressed $CdCr_2S_4$ which suggest its utility as a magneto-optic modulator in the near-ir region of the spectrum.

No measurements of the optical transmission and Faraday rotation of this ferromagnetic spinel in hot-pressed form have been previously reported. Optical transmission data on $CdCr_2S_4$ in

the near ir have been reported by Harbeke and Pinch² on single crystals of linear dimensions of about 2 mm. Their spectra indicate that the crystals have high nonintrinsic optical losses, resulting in a long-wavelength absorption coefficient of about 600 cm^{-1} . For our purposes, we define the absorption coefficient by $\alpha = 2.3D/t$, where D is the specular optical density of a sample of thickness t , corrected only for reflection loss.³ This coefficient is therefore a measure of all optical loss in the sample, excluding reflection.