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UTILIZATION OF NEAR- AND VACUUM-ULTRAVIOLET SYNCHROTRON RADIATION FOR THE EXCITATION OF VISIBLE FLUORESCENCES IN RUBY AND MgO:Cr^{3+}[†]

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(Received 16 February 1970; revised manuscript received 26 March 1970)

We report results of studies utilizing ultraviolet synchrotron radiation as a selective excitation source for the R-line fluorescence transitions of Cr^{3+} in cubic MgO and Al$_2$O$_3$. Pump bands for these fluorescences spanning the near and vacuum ultraviolet are identifiable as charge transfer bands of the CrO$_6^{3-}$ complex. We report the observation of broad bands originating from ligand-to-metal bands and terminating in $(3d)^3$ states. Comparison of the excitation spectra of the broad-band fluorescence with that of the R lines allows us to assign certain properties to the charge-transfer bands.

The infrared and visible spectra of transition-metal ions doped into ionic hosts have been extensively studied and their general behavior is well understood.[1] This is not the case for their properties in the near and vacuum ultraviolet (uv), principally because of two key difficulties[2]: (i) Normal laboratory sources are not very intense nor are they continuous throughout this region, and (ii) the host material is generally opaque to radiation at these frequencies making impurity-ion spectroscopic studies difficult, if not impossible, to conduct. The first of these empirical difficulties has been remedied by synchrotron radiation; the recent activity in the field of uv properties of solids attests to the versatility of electron storage-ring synchrotron radiation as an energy source in these hitherto experimentally difficult spectral regions.[3]

We present in the Letter results of studies where we utilized uv synchrotron radiation as a novel excitation source for visible fluorescence transitions of transition-metal ions doped into some well studied lattices, in particular, Cr^{3+} in cubic MgO and trigonal Al$_2$O$_3$. We wish to show that by monitoring the intensity of the well-known $^2E_g \rightarrow {}^4A_{2g}$ Cr^{3+} transition[4] as a function of the uv excitation frequency, we are able to probe into the energy level structure of Cr^{3+} and its neighboring anion complex far into the uv, into regions, in fact, where the host lattice is almost totally opaque to the excitation radiation. We wish to report, as well, observation of intense broad-band and sharp-line fluorescences which have not been reported previously. These fluorescences originate from high-lying metal ion and ligand complexes and allow us to assign certain properties and selection rules to charge transfer bands in Cr^{3+}.

Synchrotron radiation form the University of Wisconsin 240-MeV electron storage ring is passed through a $\frac{1}{2}$-m McPherson model 235 vacuum-uv scanning monochromator; the output is then allowed to irradiate the sample. The samples are rectangular prism shaped and are located in an evacuated chamber ($\leq 10^{-8}$ Torr) in contact with a liquid-nitrogen cold finger. Samples are placed in such a way as to expose a maximum amount of irradiated surface to a viewing port at right angle to the beam. The resulting fluorescences are analyzed through narrow-band filters or through a $\frac{1}{2}$-m Jarrell-Ash monochromator with scanning capabilities. The intensity of the radiative transition may be monitored as a function of the excitation wavelength or, by switching the uv monochromator to zeroth order, the shape of the fluorescences may be obtained. The number of photons at the output of the uv monochromator were counted directly with a

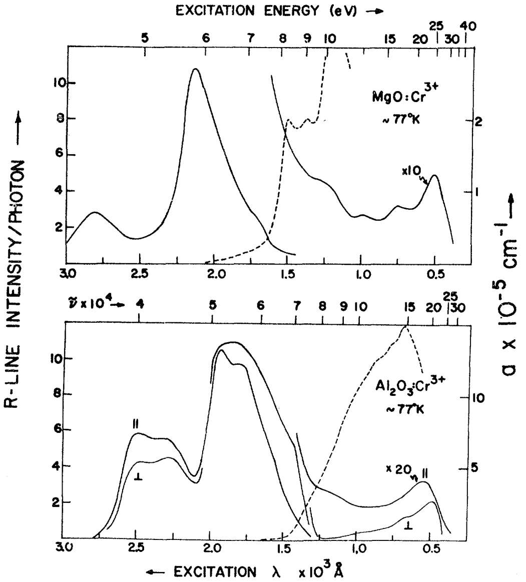

FIG. 1. Excitation spectrum for the R-line transitions in MgO and Al_2O_3. The fluorescence intensity of the R line has been normalized by dividing the measured intensity by the photon cout (see text). Polarizations for the Al_2O_3 are indicated by ∥ and ⊥ for π and σ, respectively. Dashed lines represent the lattice absorption spectrum (Ref. 7).

Channeltron multiplier. The latter is effective in the range 300-1000 Å; results of the count were extrapolated to obtain flux values at lower energy. With a ring current of 1 mA, the photon flux at 1000 Å is of the order of 10^7/Å sec.

Results for the selective excitation experiments on the $^2E\rightarrow{}^4A_2$ transitions in MgO:Cr^{3+} (0.1%) and Al_2O_3:Cr^{3+} (0.05%) are shown in Fig. 1. In the figure, the normalized R-line fluorescence intensity is plotted as a function of the excitation wavelength and energy. Two polarizations of E_{pump} relative to the crystalline c axis are shown for the case of ruby. Three distinct pump bands are apparent in the figure for both lattices. For MgO:Cr^{3+}, the main peaks fall at 2815, 2120, and 510 Å with structure appearing between the last two bands. For ruby, the excitation spectrum is polarization dependent; peaks occur at 2470, 2325, 1925, 1800, and 560 Å in σ ($E\perp c$) and at 2490, 2280, 1875, and 500 Å in π ($E\parallel c$).

The lowest energy bands, at 2815 Å (35 525 cm^{-1}) in MgO and at 2470 Å (40 485 cm^{-1}) and 2490 Å (40 160 cm^{-1}) in Al_2O_3, are readily identifiable as the $^4T_{1g}(^4P)$ state in cubic coordination or its components in a trigonal field. The positions reported here agree well with published results[1,5]; the oscillator strength of this state is said to be roughly comparable with that of the $^4T_{2g}(^4F)$ absorption band of Cr^{3+} in the green. Our results would seem to indicate that the pumping efficiency in the near uv (1500-3000 Å) for conversion to R-line fluorescence is equivalent to, if not larger than, that of the blue-green bands of chromium [$^4T_{1,2}(^4F)$]. As we shall see, other considerations shall enter to affect the absolute efficiency.

We attribute the remaining bands (Fig. 1) in both lattices to charge-transfer transitions involving the Cr^{3+} ion and its neighboring anion-ligand complex. The peaks in the vicinity of 50 000 cm^{-1} arise from ligand-to-metal ion orbital transitions, in which an electron which is localized in an anion ligand is promoted to the central transition-metal ion.[6] In the molecular orbital picture, the Cr^{3+} ion in octahedral coordination is treated with its six near-neighbor oxygen ions as a single $CrO_6{}^{3-}$ complex. The charge-transfer transitions then entail promotion of electrons from occupied p orbitals [$t_2(\pi)$, $t_1(\pi)$] to unoccupied d orbitals [$e_g(\sigma^*)$, $t_{2g}(\pi^*)$]. We can also conclude tentatively that this band peaking at 2120 Å for MgO:Cr^{3+} involves the $t_{1,2}(\pi)$ orbital states. It is apparent from Fig. 1 that the lower-symmetry field of Al_2O_3 splits this transition into three fairly well resolved bands which are polarized. Studies of the effects of trigonal distortions on metal-ion–ligand complexes are in progress at this time.

The excitation peaks in the vicinity of 180 000 cm^{-1} in both lattices may be attributed to metal ion–to–metal ion transitions in which an electron is promoted from a $3d$ orbital to an unoccupied $4p$ state. Such transitions are both spin and parity allowed and have their origin at, and thus may be correlated to, the free-ion $4p$ state located at 160 000-175 000 cm^{-1}. Charge-transfer processes may also be involved; however, because of smaller overlap of wave functions, they are weaker than metal-to-metal transitions.

We have plotted in Fig. 1 the lattice absorption coefficient whenever available.[7] It is evident that above 60 000 cm^{-1}, only a small fraction of the total Cr^{3+} impurity content is exposed to the excitation. The rapid decrease in fluorescence efficiency in this energy region indicates that energy transfer processes between host and Cr^{3+} complex are probably negligible. Closer analysis of the excitation spectra and pump-band shapes support this conclusion. In MgO, the minima in the structure between 75 000 and 135 000 cm^{-1} (at 76 920, 95 240, and 112 360 cm^{-1}) correspond to the maxima of the lattice absorption coefficient; it would appear from our results that a fourth absorption maximum occurs at 160 000 cm^{-1} or 19.8 eV in MgO. No pronounced features appear in the absorption coefficient of Al_2O_3, consequently a fairly smooth excitation band is observed above 75 000 cm^{-1}. The abrupt cutoff of the σ band at 53 335 cm^{-1} corresponds to an observed rapid increase in the absorption coefficient of the host corundum.

Compensating for the rapid attenuation of the ultraviolet excitation, allowed charge-transfer processes have extremely large oscillator strengths. That uv pumping leads to a visible signal at the R-line frequency at all bears witness to the strengths of these transitions. That excitation results throughout the vacuum ultraviolet suggests the existence of various ligand-to-metal and metal-to-metal transitions which are being obscured by interband transitions of the host. Nevertheless, it should be feasible to obtain strength measurements for these transitions by folding the lattice attenuation into the excitation spectrum. An extremely rough estimate of the oscillator strength of the 178 570 cm^{-1} band in ruby leads to an f value ~1.0.

We report in this Letter observation of broad-band fluorescences which have not been reported previously. We believe that these fluorescences originate from charge-transfer states of the Cr^{3+}-ligand complex and terminate in the $(3d)^3$ crystalline field states. The fluoresence of MgO:Cr^{3+} when pumped with broad band uv radiation is shown in Fig. 2(a) and consists of two broad bands peaking in the neighborhood of 30 000 and 19 000 cm^{-1}, respectively. The selective excitation spectra for the two components of the fluorescence of MgO:Cr^{3+} are shown in Fig. 2(b).

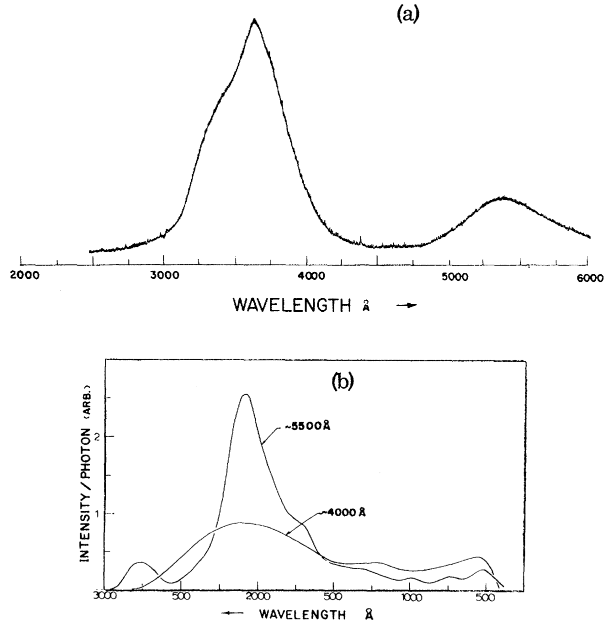

FIG. 2. (a) Observed broad-band and sharp-line fluorescence in MgO:Cr^{3+} at ~77°K; spectrum is not corrected for instrument response. (b) Excitation spectra for ~4000- and ~5500-Å fluorescences in MgO doped with Cr^{3+} at ~77°K.

Comparison of the excitation spectra represented in Figs. 1 and 2 allows us to draw certain conclusions regarding charge-transfer bands and to assign to them certain properties and selection rules. Our conclusions are diagrammed in Fig. 3 where we have summarized our observations for the case of MgO.

We believe that a spin quantum number may be

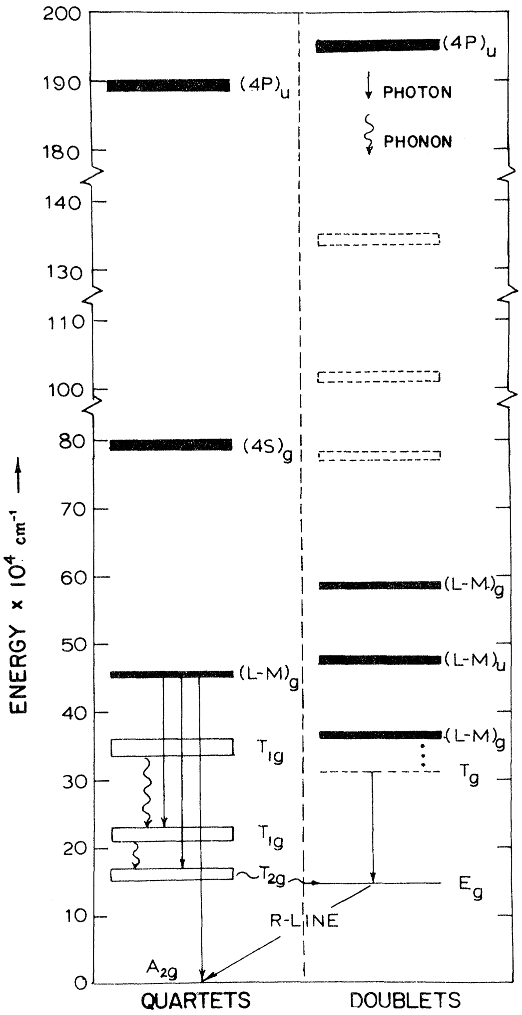

FIG. 3. Energy-level and relaxation scheme for Cr^{3+} and Cr^{3+}-ligand complex in MgO.

adequately assigned to each charge transfer band. The complexes thus may be classified into quartets and doublets which to first, and perhaps higher, order obey spin selection rules. In terms of Fig. 3, in other words, no first order lateral transitions occur between columns at the charge-transfer energies. We have also tentatively assigned parity properties to each complex on empirical oscillator strength considerations.

From the excitation spectra [Fig. 2(b)], the two bands which fluoresce in MgO:Cr^{3+} originate from different ligand-to-metal states. The band centered at ~5500 Å [Fig. 2(a)] appears to originate from a complex located at ~35 000 cm^{-1}. Termination at the $^4T_2(^4F)$ state of Cr^{3+} yields, to within the width of the band, the appropriate observed fluorescence energy. The excitation bands associated with this transition may thus be assigned to a quartet spin configuration.

Similarly, the near-uv band fluorescence originates at ~45 000 cm^{-1} and terminates in the $^2E(^2G)$ state; again the excitation bands can be assigned a doublet spin label. The principal excitation band, which by definition involves the ^4A ground state, is fairly weak in this case; this lends some credence to our spin and parity assignment. We believe that this state probably involves the promotion of electrons from the p-like $t_{1g}(\pi)$ and $t_{2g}(\pi)$ orbitals to unfilled d states. It has been noted that the $^2E_g(^2H)$ state also lies in this region and the strength of this fluorescence may also arise from a $^2E \rightarrow {}^2E$ transition.[5,8]

Analogous fluorescence and excitation spectra are observed in the case of ruby. The fluorescence bands are shifted to higher energies and the trigonal field in Al_2O_3 appears to lend considerable strength to the excitation bands particularly in the case involving the doublets. From Fig. 2(b), it is also evident that the strong odd quartet ligand-to-metal states at ~50 000 cm^{-1} do not contribute to the doublet fluoresences, giving further justification for our quartet and doublet classification, and indicating that phonon-induced crossover is either negligible or exceedingly slow in this case even though energies involved are not forbidding. The even quartet state responsible for the ~5500-Å fluorescence seems to be stable against phonon relaxation as well; for the very presence of radiation from this state indicates slow nonradiative decay to the nearby $^4T_1(^4P)$ state. That this is the case is not entirely surprising; the relaxation is in effect a metal-to-ligand transition. On the basis of overlap considerations, we expect it to occur at a slower rate than corresponding phonon induced metal-to-metal transitions.

Sharp line spectra other than R-line fluorescence occurring in the vicinity of ~5000 Å are sometimes observed in both MgO:Cr^{3+} and ruby. Unfortunately, these lines are nonreproducible and must await further investigation to determine their origins.

Finally, the R-line excitation spectrum (Fig. 1) consists of the superposition of (i) the population of the ^2E level through the doublet system and (ii) excitation of the quartet levels and phonon relaxation to the ^2E through the ^4T states. These results are relevant in the analysis of ruby laser operation when pumped with enhanced ultraviolet components.

In concluding, we believe that we have obtained a feasible energy-level scheme for the so-called charge-transfer complexes of the Cr^{3+} ion by exploiting the availability of uv radiation in a simple way. The use of electron storage-ring radiation appears to give us a powerful new technique to delve into impurity-ion processes in uv regions of the spectrum and extension of this study to other ions, such as the $4f$ series, and other lattices seems to us to be highly worthwhile. Utilization of the strong fluorescences originating from high-lying complex bands as a possible laser source would seem feasible at this time. It is our hope that these results will stimulate activity in considering the theoretical problems encountered here.

We wish to express our appreciation for the cordial cooperation rendered to us by the staff of the Physical Sciences Laboratories, particularly F. E. Mills, C. Pruett, and E. Rowe. The uv monochromator was made available to us through the kindness of Professor H. Fritzsche and his University of Chicago group. Comments from and discussions with Professor D. S. McClure, Professor A. L. Schawlow, and Professor R. N. Dexter are gratefully acknowledged. We wish to acknowledge with thanks the able assistance of Dr. M. Y. Chen in commenting on the manuscript.

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†Synchrotron facilities at the Physical Sciences Laboratories, University of Wisconsin, supported by U. S. Air Force Office of Scientific Research under Contract No. F44620-70-C-0029.

*On leave from Instituto Geofísico del Perú, Lima, Perú.

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f-SUM RULE ANALYSIS OF THE BAND EDGES IN PbS, PbSe, AND PbTe

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(Received 30 March 1970)

The f-sum rule is applied to the conduction- and valence-band edges at the L point in PbS, PbSe, and PbTe. Experimental values of the energy gaps and electron and hole effective masses for PbS and PbSe follow the f-sum rule while those for PbTe do not. It is proposed that the well-known anomaly in the relative values of the energy gap of these semiconductors is due to an irregular value for PbTe.

The experimentally measured values of the energy gap E_G for PbS, PbSe, and PbTe exhibit a well-known anomaly. Recently determined values[1] of these energy gaps at 4.2°K are as follows: for PbS, $E_G = 0.286 \pm 0.003$ eV; for PbSe, $E_G = 0.165 \pm 0.005$ eV; for PbTe, $E_G = 0.190 \pm 0.002$ eV. These values of the energy gap do not exhibit the common monotonic decrease of E_G with increasing atomic number of the atom X in a compound semiconductor MX. Examples of this decrease are observed in the values[2] of E_G at 4°K in the sequences InP ($E_G = 1.416$ eV), InAs ($E_G = 0.425$ eV), InSb ($E_G = 0.236$ eV), and GaP ($E_G = 2.325$ eV), GaAs ($E_G = 1.517$ eV), GaSb ($E_G = 0.813$ eV). This Letter reports an examination of the band edges in the sequence PbS, PbSe, PbTe and concludes that PbTe is the anomalous member of the sequence.

In order to examine the energy-gap sequence in the lead-salt semiconductors, the f-sum rule[3] was used. This relation, for the L point of the Brillouin zone of the face-centered-cubic lattice, is

$$\left(\frac{m}{m^*}\right)_{ij} = \delta_{ij} + \frac{2}{m}\sum_n{}' \frac{\langle p,L|\pi_i|L,n\rangle\langle n,L|\pi_j|L,p\rangle}{(E_{p,L}-E_{n,L})}. \tag{1}$$

In Eq. (1), $(m/m^*)_{ij}$ is the ijth component of the effective-mass tensor at the point L of the band p, δ_{ij} is the Kronecker delta, m is the free-electron mass, p and n are band indices, L denotes the L point, and $E_{p,L}$ and $E_{n,L}$ are the energies of the bands p and n, respectively, at the L point. The summation is over all bands n which interact with band p, and π_l is the lth component of the quantity $\vec{\pi}$ defined[4] by $(\vec{\pi}\cdot\vec{k}) = mH'$, where H' is the perturbation used in $(\vec{k}\cdot\vec{p})$ theory; in this case the Hamiltonian for $k = L$ is taken as the unperturbed Hamiltonian.

Consider first the simplest band model defining the energy gap in the lead compounds, in which the f sum includes only two bands: Band p is the lowest conduction band (L_6^-) and band n is the highest valence band (L_6^+). Then $(E_{p,L}-E_{n,L}) = E_G$, the energy gap. For these semiconductors, the surfaces of constant energy (for both holes and electrons) are prolate ellipsoids of revolution characterized by two effective masses: a transverse mass m_t and a longitudinal mass m_l. For both m_t and m_l, $i = j$ since there are no off-diagonal terms, and M is the matrix element involved; Eq. (1) then becomes $m/m^* = 1 + (2/m)(|M|^2/E_G)$, where m^* is either m_t or m_l. Rearranging gives

$$m^*/(m-m^*) = (m/2|M|^2)E_G. \tag{2}$$

Equation (2) shows that for this simple two-band model $m^*/(m-m^*)$ is proportional to E_G, and the linear plot of $m^*/(m-m^*)$ as a function of E_G