

(blue-green), where the cobalt ion also is surrounded by six oxygen ions (distorted octahedron),² that Dq is about 690 cm^{-1} and B is about 770 cm^{-1} , even though the cobalt-oxygen distances are quite comparable. We relate the change in Dq from 920 to 690 cm^{-1} to the effect of the tungsten ion, which reduces the net charge on the oxygen ion relative to the oxygen in MgO .

Second, we have measured the absorption spectrum of the Ni^{2+} ion in MgWO_4 (orange). Here we find that Dq is again lower than for nickel ion in MgO (green), 710 and 860 cm^{-1} , respectively, and B is again lower in the tungstate.

Third, we have measured the absorption spectra of K_2NaCrF_6 (dark green) and CrF_3 (yellow green). In both of these crystals the chromium ions are surrounded by octahedra of fluoride ions, but the next nearest neighbors are different.³ In K_2NaCrF_6 each fluoride ion is shared linearly by chromium and sodium ions, while in CrF_3 (quite unlike CrBr_3 and CrCl_3) each fluoride ion is shared by two chromium ions at an angle of 146° . The room temperature data given in Fig. 1 show the striking difference between the two crystal spectra. The spectrum of K_2NaCrF_6 fits the theoretical energy level diagram⁴ with $Dq=1650\text{ cm}^{-1}$ and $B=680\text{ cm}^{-1}$. However, values of $Dq=750\text{ cm}^{-1}$ and $B=920\text{ cm}^{-1}$ (free-ion value) are needed to fit the spectrum of CrF_3 . Since the $\text{Cr}-\text{F}$ distances are the same within experimental error, these observations are again related to the effect of next nearest neighbors. Note that for Cr^{3+} the lower Dq goes with a higher B value, while for Co^{2+} and Ni^{2+} the lower Dq is accompanied by a lower B value.

The following consequences of these results are important for both empirical and theoretical developments of ligand field theory. First, the spectrochemical series of ligands,⁵ derived from solution spectra, does not apply to ionic crystals if there is a change of structural type, and arguments relating absorption spectra to structure are not generally valid for solids when based on this series alone. Second, there is no doubt that the changes of the Racah parameter B from the free ion value mean that a molecular orbital rather than an atomic orbital formulation for the interelectronic repulsion terms is needed, but we feel that even with this model, the physical interpretation of the variations in the B parameter in terms of so-called "covalency effects"⁶ should be viewed with some caution. Last, the polarization of the ligand orbitals by the metal ion and next nearest neighbors is an important factor determining the magnitude of the crystal field splitting.

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Absorption Spectrum of Gaseous Cl^- and Electron Affinity of Chlorine

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WE wish to report observations of ultraviolet absorption spectra of several alkali halide vapors heated by shock waves. Spectra have been taken of RbF , RbBr , CsF , and CsCl . With the chloride salts, we find continuous absorption which we attribute to the gaseous ion Cl^- , undergoing the process $\text{Cl}^- + h\nu \rightarrow \text{Cl}^0 + e^-$. This continuum has the two sharp thresholds expected for photodetachment¹ and permits determination of the electron affinity of chlorine with considerable precision.

The shock tube is conventional. The driver section (155 cm), is separated from the low-pressure section (460 cm) by a scored aluminum diaphragm; both have the same square inside cross section (8.5×8.5 cm). Shock speeds are measured with platinum thermal-resistance gauges painted on glass rods located 197, 222, and 247 cm downstream from the diaphragm, and with a photocell at the quartz observation windows, 357 cm from the diaphragm. Signals are monitored on an oscilloscope (Tektronix 533) triggered by the shock passing the first gauge. The spectral source is a quartz capillary flash lamp which is fired by a "crowbar" trigger (KU 402), operated by a delayed signal from the oscilloscope. The mirrors of a White multiple-reflection system² mounted outside the shock tube are adjusted to give four traverses; the optical path is thus approximately 34 cm. A Bausch & Lomb medium quartz spectrograph is used with Kodak 103-0 plates.

Salt samples (0.1–1.0 g) are introduced into the shock tube as dried deposits on strips of cellulose tissue or on thin perforated aluminum foil, which are placed across the shock tube about 90 cm upstream from the observation windows. The low-pressure gas is argon at pressures of 1.5 to 2.5 cm Hg. Hydrogen is the driver gas; driving pressures fall between 200 and 350 psi. Resulting shocks have velocities of Mach 8.5–9 before reaching the sample. The most intense absorption has come with the strongest shocks.

In all cases comparison spectra of the flash lamp have been taken. In later work, each plate has included the spectrum of a shock through the supporting material alone. When tissue is used we observe absorption by C_2 , OH, and possibly CH. Aluminum gives atomic lines. Spectra of shock-heated alkali halide vapors display the principal series of the alkalis; we have definitely observed the rubidium series to 14μ , and the cesium series to 16μ . Especially with large samples, higher members of the series are quite broadened.

The rationale for expecting large negative ion concentrations comes from the equilibrium constants for the processes $MX \rightarrow M^+ + X^-$ and $MX \rightarrow M^0 + X^0$. At $4000^\circ K$, dissociation constants (atm) to ions are 1.453×10^{-4} , 9.61×10^{-4} , 1.934×10^{-4} , and 6.62×10^{-4} , for RbF, RbCl, CsF, and CsCl, respectively; concentration ratios of dissociated ion pairs to atom pairs are 1:58, 1:39, 1:24, and 1:16.5 for the same species. Therefore, one expects a large equilibrium concentration of negative ions, particularly for chloride in CsCl vapor. The problematical quantity is the magnitude of the extinction coefficient of chloride ion near its threshold.

In the case of both the chloride salts, two sharp decreases in plate density appear, at 3424 and 3325 Å. These are apparent on the tracings and plots of differences between plate densities of salt spectra and comparisons, and are quite obvious to the eye. The intensity of the continuous absorption is significantly greater for CsCl than for RbCl, under similar conditions. Measurements so far have not been sufficiently precise to say whether the slope of absorption is infinite at the thresholds, but it is certainly extremely steep, rising well above noise level over a range of less than 10 Å. The intensity also correlates well with the intensities of the alkali absorption lines. With fluorides or bromides, or with the various comparison spectra, these sharp intensity changes have not been detected. Crude measurements indicate that the relative intensity of the two absorption steps is independent of shock strength and sample size.

Photodetachment of an electron from Cl^- can leave the chlorine atom in either of two states, $^2P_{3/2}$ or $^2P_{1/2}$. The separation between these levels is 0.1092 eV.³ The absorption thresholds we detect are at 3.620 and 3.728 ± 0.007 eV; the separation of 0.108 eV is therefore in agreement with the spin-orbit splitting of chlorine.

The conditions under which the absorption is found, its two sharp thresholds with their seemingly constant relative intensity, and the energy separation between the thresholds all lead us to assign the spectrum to the photodetachment process of the chloride ion. The lower threshold therefore falls at an energy equal to the electron affinity of chlorine. With a Debye-Hückel correction of 0.7 ± 0.4 kcal/mole for the presence of other ions, the value we obtain is 84.2 ± 0.4 kcal/mole. Other recent values fall from 86.7 ± 2 to 85.1 kcal.

Continua due to other negative ions are under

investigation now. We are also conducting measurements aimed at determining relative extinction of the chloride spectrum.

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Fe^{57} Mössbauer Effect in Laves Phases Containing Fe Combined with Y, Ce, Ho, Ti, Zr, and Hf

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RESONANT absorption of γ rays by Fe^{57} (Mössbauer effect) has been used to determine the nuclear hyperfine field (H_i), quadruple splitting (ϵ), and the center shift (ΔE) for a number of Laves phases. The samples examined were those in Table I plus $HoFe_2$, $HfFe_2$, and several other $TiFe_2$ - $ZrFe_2$ solid solutions. Magnetic examination indicated that most of the samples studied are ferromagnetic at or slightly below room temperature.¹ This is not the case for $TiFe_2$ and the hexagonal $TiFe_2$ - $ZrFe_2$ alloys, which exhibit temperature independent paramagnetism² down to $2^\circ K$, nor for $HoFe_2$, whose magnetic behavior is complex.¹

Results obtained are summarized in Table I. Before commenting on specific results, some general remarks concerning the experimental observations and results cited seem appropriate. First, for the ferromagnetic materials the quadrupole splittings have not been determined. The hyperfine spacings seemed to be unequal, thus resembling in general the observations of Kistner and Sunyar³ for Fe_2O_3 and suggesting a non-vanishing quadrupole interaction. The inequalities were, however, comparable with the uncertainties in line positions and hence no attempt was made to