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Optical Absorption Spectrum of AgF

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The optical absorption of thin films of silver monofluoride has been investigated in the visible and ultraviolet region of the spectrum at room and low temperatures. Exciton peaks have been observed at 4.63 and 6.34 eV for samples at 4.8 °K. The first exciton peak is considerably lower in energy than might be expected on the basis of the trend set by the other silver halides. This unusually low energy has led us to speculate that the band structure of AgF may be quite different from those of the other silver halides.

I. INTRODUCTION

Although the optical absorption spectra of the common silver halide crystals (i.e., AgCl, AgBr, and AgI) have been studied extensively,[1] no information has been reported on the absorption spectrum of silver monofluoride crystals. This omission is related to various untoward properties of silver monofluoride which cause its preparation in a pure state to be difficult. Like the other silver halides it is sensitive to light, but unlike the other silver halides it is hygroscopic and highly reactive, and decomposes on melting. Moreover, three different fluorides of silver are known to exist[2]—silver monofluoride (AgF), silver subfluoride (Ag_2F), and silver difluoride (AgF_2).

One of the few published studies on AgF was of its gas-phase absorption spectrum, in which the 0, 0 energy and vibrational constants of the $^3\Pi_0^+ \leftarrow {}^1\Sigma$ transition were determined.[3] These constants were compared with those of AgCl, AgBr, and AgI, and were found to be in accord with the trends set by the other three members of the series. In the gas phase, however, the silver halides are expected to act as diatomic molecules; thus, this study provides little insight into the optical properties of AgF crystals.

The present study of the visible and ultraviolet absorption spectrum of AgF was undertaken on thin films. The observed optical spectrum of AgF differs significantly from predictions based on simple considerations of the spectra of the other silver halides. We discuss the unusual behavior found in terms of the theoretical framework available at present.

II. EXPERIMENTAL

Thin films of AgF were prepared from commercially available silver monofluoride using a fractional evaporation technique in vacuum under red light. The silver monofluoride starting materials obtained from a number of sources varied in color from yellow to black, and were always contaminated with silver, silver oxide, water, and various trace impurities. A particular sample of chemically pure grade AgF, purchased from the Amend Drug and Chemical Co., Inc., was found to be relatively pure and was used in these studies. Analysis of this commercial sample by flame emission spectroscopy, together with spark-source mass spectroscopy, showed the major trace impurities listed in Table I. In one case where the AgF had contacted glass, additional impurities of silicon, calcium, and the alkali metals were found. The films were formed by evaporating the dried commercial AgF sample from a pyrolitic graphite boat at a rate of approximately 0.05 μ/h. At faster deposition rates, large amounts of colloidal silver were often formed in the evaporated layers. The film thickness was measured by a Sloan thickness monitor[4] and by x-ray fluorescence studies of the silver in the film.

The AgF films were deposited on single-crystal CaF_2 substrates which were held at about 80 °C during evaporation. Analysis of the films by spark-source mass spectroscopy indicated that they generally contained a level of trace impurities similar to that found in the commercial AgF starting material. Visual examination of the films showed them to be colorless, presumably indicating that the concentration of colloidal silver and other colored impurities was substantially reduced. An investigation of the layers by x-ray diffraction showed them all to be crystalline and highly oriented, with the (111) planes parallel to the surface of the CaF_2 substrate. The orientation of the AgF film was due

TABLE I. Major trace impurities in commercial AgF (in ppm).

Al	Br	Cl	Cu	Fe	Pb	Mg	Ni	Na
20	4	50	40	10	3	3	1	20

to epitaxial growth on the surface of CaF_2 single crystals whose (111) planes were within (12 ± 1)° of being parallel to the surface. The x-ray pattern indicated the presence of Ag_2F in many of the evaporated AgF films. In highly oriented AgF films (e.g., 98% oriented) which were used to obtain the spectra, 1% or less of Ag_2F was found.

The AgF films were stored and handled in the dark under a nitrogen atmosphere. The samples were placed in a Teflon-coated metal sample holder and transferred to the precooled Dewar. Extreme care was taken to prevent the samples of AgF from being exposed to light or moisture. In some of the first experiments it was found that the AgF films decomposed slowly in the beam of the spectrometer as it scanned the ultraviolet region, so in subsequent work care was taken to minimize the exposure of the samples to short-wavelength radiation.

All spectra shown were taken in an Andonian throttle valve-type liquid-helium Dewar equipped with quartz optical-access windows. The sample temperatures were measured with a calibrated germanium resistance thermometer. The spectra were recorded on a Cary Model 14 spectrometer, and small corrections were made for the absorption of the quartz windows of the Dewar and the CaF_2 substrate. Calibrated neutral-density filters were used in the reference beam, allowing optical densities as large as four to be recorded. The instrumental resolution was better than 3 Å from 8000 to 2200 Å, whereas, from 2200 Å, the resolution decreased to about 20 Å at 1950 Å.

A constant correction factor was applied to the entire spectral region to account for the reflection loss of the AgF films due to the real part of the refractive index, although the true absorption coefficient in the region of high absorption is probably lower than calculated. Corrections to several of the observed spectra were also made for the absorption of colloidal silver in the region 4100–5500 Å. This correction was made by allowing a AgF film to hydrate in the cryostat, thus destroying the weak AgF absorption in the vicinity of the colloidal silver absorption. A weak band of unchanged optical density (OD)(i.e., OD = 0.05) which peaked at ca 4700 Å was left by this procedure, and this band is presumably due to colloidal silver.[5] The band was then subtracted from the spectra previously determined on the unhydrated AgF film.

TABLE II. Lattice constants of silver halides with the NaCl structure.

Compound	a_0(Å)
AgF	4.936 ± 0.001[a]
AgCl	5.550 23 ± 0.000 05[b]
AgBr	5.774 75 ± 0.000 05[b]

[a]References 6 and 7.
[b]Reference 9.

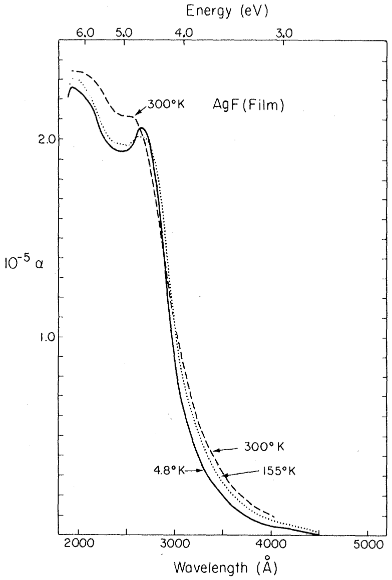

FIG. 1. Absorption spectrum of AgF at 4.8, 155, and 300 °K; α vs wavelength.

AgF crystallizes in the cubic space group $Fm3m(O_h^5)$ which is a NaCl-type structure.[6,7] This is the same space group to which AgCl and AgBr

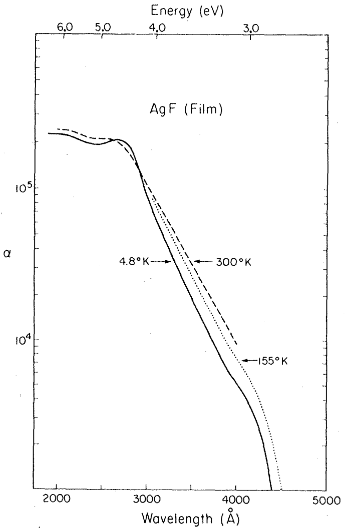

FIG. 2. Absorption spectrum of AgF at 4.8, 155, and 300 °K; log α vs wavelength.

TABLE III. Transition energies and refractive indices of the silver halides.

	Direct transitions		Indirect transition	
Compound	Γ (eV)	*L* (eV)	(eV)	η_∞
AgF (4.8 °K)	4.63 ± 0.02[a]	6.34 ± 0.15[a]	2.8 ± 0.3[a]	1.73[b]
AgCl (20 °K)	5.10[c,d]	6.25[c,d]	3.25[c,d]	1.980[e]
AgBr (20 °K)	4.25[c,d]	6.1[c,d]	2.68[c,d]	2.149[e]

[a] This work.

[b] Calculated in this work.

[c] Reference 1.

[d] References 10 and 11.

[e] Reference 12.

belong[8,9]; the lattice constants for the isomorphous silver halides are listed in Table II.

III. RESULTS

The spectrum of AgF is shown in Figs. 1 and 2 at several temperatures. There are two peaks observed in the region of strong absorption. The energies of these peaks are collected in Table III along with other relevant data for comparison.

The lowest-energy peak has been assigned to a Γ exciton absorption (Γ_{15} to Γ_1) in analogy with what has been calculated for AgCl and AgBr.[10,11] Similarly, we assign the second strong transition to an *L* exciton absorption.[10,11] The expected spin-orbit splitting for fluorine is much too small to be observed in these spectra.[13] In fact, it is noted that the AgF spectrum is somewhat broader than the spectra of the other silver halides at low temperatures. This trend for broadness is also found in the alkali fluorides, whose spectra are notably broader in the region of the first exciton transition than those of corresponding chlorides, bromides, and iodides at low temperature.[13]

The value for the refractive index at infinite wavelength given for AgF in Table III was deduced using the method of Tessman *et al.*,[14] together with the recent refractive index and lattice constant data for the other silver halides listed in Tables II and III. The reflection loss computed using the refractive indices is about 8% of the incident light. This agrees with the observed reflection loss in highly oriented AgF films where the scattering due to crystal imperfection is negligible.

The effects of disorder and/or the addition of a small amount of Ag_2F to the sample have been observed. One sample was > 98% ordered and contained less than 1% Ag_2F. The other sample was ~60% ordered and contained ~5% Ag_2F. A small effect is noted at energies just below the first exciton peak where the ordered sample decreases in optical density more rapidly than the disordered sample. No absorption ascribable to Ag_2F was found.

IV. DISCUSSION

A. Direct Transition

Although the silver fluoride spectrum resembles the spectra of the other silver halides generally, there is one important difference which requires discussion. From Table III we note that the energy of the first exciton peak of silver fluoride lies about halfway between the exciton energies for silver chloride and silver bromide. This observation conflicts with the trend in exciton energies expected from a simple consideration of the silver halide ion separations based on lattice constants.[15]

To examine further this apparent contradiction, a somewhat more elaborate estimate of the exciton energies has been made using the method outlined by Mott and Gurney.[16] For the alkali halides, values calculated by this approach are usually about 2 eV higher than the measured values. This discrepancy arises because the interaction between the alkali atom and its environment has been neglected in the calculation. It has been shown that in the group-I*A* alkali halides, the calculated exciton energy trends follow the observed spectral data closely.[16] A comparison of the calculated values given in Table IV with the observed values listed in Table III shows that the expected trend is not followed in the cubic silver halides. The reason for this anomalous behavior is not understood at present; extensive band-structure calculations are needed to elucidate it.

One might speculate that the 4.63-eV exciton transition in AgF is not of the Γ type. If the silver *d* band lies above the halogen *p* valence band, the 4.63-eV absorption might be due to the upward bending near *X*, *L*, or Δ.[21] Indeed, it may be an *X* exciton in analogy to certain band predictions of[22] CsF and alkaline-earth fluorides.[23] In accord with this speculation we note that the temperature dependence of the first exciton peak in AgF is signifi-

TABLE IV. Estimation of the lowest exciton energies for the cubic silver halides.[a]

	I(Ag)[b]	$E(X)$[c]	$\frac{(2\alpha-1)e^2}{r_0}$	ψ_{pol}[d]	$(h\nu)_{calc}$
AgF	7.574	3.464	14.56	2.28	8.17
AgCl	7.574	3.649	12.93	2.49	6.52
AgBr	7.574	3.515	12.42	2.61	5.76

[a] All energies are in eV (Ref. 16), and

$$(h\nu)_{calc} = \frac{(2\alpha-1)e^2}{r_0} + E - I - \psi_{pol},$$

where E is the electron affinity, I is the ionization potential, α is the Madelung constant, and ψ is the polarization energy.

[b] Reference 17.

[c] References 18 and 19.

[d] Reference 20; $\alpha_{F^-} = 0.759$, $\alpha_{Cl^-} = 2.974$, $\alpha_{Br^-} = 4.130$, and $\alpha_{Ag^+} = 2.115$.

cantly different than those of the other silver halides.[1,17] The peak at 6.34 eV could then correspond to the Γ exciton transition and this energy would then be in agreement with the simple predictions previously mentioned.

B. Indirect Transition

The thickness of the films available to us does not allow any thorough investigation of the indirect absorption and our method of subtracting out the absorption due to colloidal silver leaves some question as to the exact shape of the spectrum beyond 4000 Å (see Fig. 2). One can, however, make some general statements and inferences. It does seem certain that the indirect edge lies at wavelengths longer than 4000 Å. The data do indicate that the indirect edge is in the vicinity of 4400 Å (2.8 eV), and the shape and absorption coefficient of the suspected indirect transition are very similar to those of the other silver halides.[17] These data are also found in Table III along with values for the other silver halides.

Here again the data for AgF are found to fall between those for AgCl and AgBr. This decrease in the energy of the indirect transition might have been anticipated on the basis of an increase in the *p-d* mixing at L_3, but this does not seem to be the whole answer. Indeed, the question of the energy of the indirect absorption and the first exciton absorption depends more realistically on the relative positions of the valence and conduction bands at the zone center.

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