

S.I.A. model the C_{xxz} is always positive. Table II shows that C_{xxz} for HoFeO_3 , DyFeO_3 , TbFeO_3 , GdFeO_3 , EuFeO_3 and C_{zzx} for SmFeO_3 is indeed negative, indicating that the dominant mechanism in the orthoferrites is the A.S.E. one. An additional point that rules out the S.I.A. mechanism even in YbFeO_3 , TmFeO_3 and ErFeO_3 in which C_{xxz} is positive, is the high value of the anisotropy constant ($K \approx 15 \times 10^8$ erg/mole), which is larger than that expected for Fe^{+3} ion in a similar configuration.¹⁴

The calculated coefficients C_{yyz} for both mechanisms are practically equal and lower than the sensitivity threshold of the torquemeter. Although C_{yyz} in some of the materials appears to be higher than the predicted ones, because of the low measured values and their large spread, no significant conclusions can be drawn.

The ions of Gd^{3+} have a basic level 8S , lie on an approximately cubic lattice and are therefore isotropic.³ It can be assumed that in GdFeO_3 the anisotropy in the

susceptibility is due mostly to the iron ions. Evidence to this assumption is the isotropy of the susceptibility in the plane perpendicular to the antiferromagnetic axis, in contrast to the other orthoferrites with paramagnetic rare earth. One can then use the measured anisotropy of the susceptibility in GdFeO_3 as an additional check for the dominant mechanism. Experimentally (see Table II) $\chi_x > \chi_z$. This is inconsistent with the S.I.A. model as shown from Table I.

According to the A.S.E. model this relation between the susceptibilities occurs for $\sigma_0^3 D^2 / 4K_b H_e > 1$ which is actually the case in GdFeO_3 , as can be seen from Table III. This is an additional evidence that the dominating mechanism is the A.S.E. one.

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F Band in Isotopically Enriched LiF^\dagger

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The effect of isotopic composition on the optical absorption spectrum of the F center in LiF has been investigated. The results of measurements on single crystals of x-ray irradiated Li^6F (almost 96% lithium-6) and Li^7F (almost 100% lithium-7) indicate that the average F -band width at half-maximum in the former is larger by about 3% at liquid-helium temperature, and by about 1% at room temperature. Theory shows that the half-widths in the two isotopic forms vary inversely as the fourth root of the mass of the alkali ions at low temperature, and as the temperature is increased the predicted half-width difference monotonically decreases to zero. The predicted half-width difference at low temperatures is about 4%, and at room temperature about 1%, both in reasonable agreement with experiment. At both room and liquid-helium temperatures the position of the F -band maximum in Li^7F is slightly displaced to higher energy than in Li^6F . The peak-position shift is in approximate agreement with the contributions arising from the difference in alkali mass and lattice constant of the two crystals as estimated at low temperature.

I. INTRODUCTION

THE F center, an electron bound to an anion vacancy, has been the subject of numerous experimental and theoretical studies in alkali-halide crystals.¹⁻⁷ The principal transition of the F center from its

[†] A preliminary account of this work was presented at the New York American Physical Society Meeting, January 1964, Bull. Am. Phys. Soc. 9, 89 (1964).

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¹ R. W. Pohl, Proc. Phys. Soc. (London) 49, 3 (1937), extra part.

² F. Seitz, Rev. Mod. Phys. 18, 384 (1946).

³ F. Seitz, Rev. Mod. Phys. 26, 7 (1954).

⁴ D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

⁵ J. J. Markham, Rev. Mod. Phys. 31, 956 (1959).

⁶ B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

⁷ J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

ground state gives rise to the well-known F -band absorption. This band is approximately Gaussian in shape, and its spectral location is characterized by the particular crystal, typically occurring in the visible or ultraviolet ranges. Normally, half-widths of the F band are found in the range 0.4–0.7 eV in the vicinity of room temperature. Upon lowering the temperature there is appreciable narrowing of the bandwidth and shifting of the spectral position of the band maximum to higher energies. The breadth of the F band is attributed to interaction with vibrational modes of the lattice, and even at low temperature the F band retains appreciable half-widths, normally over 50% of the room-temperature value, owing to zero-point vibration of the lattice.

The interaction of the F center with vibrational phonons has been treated theoretically in the limit of

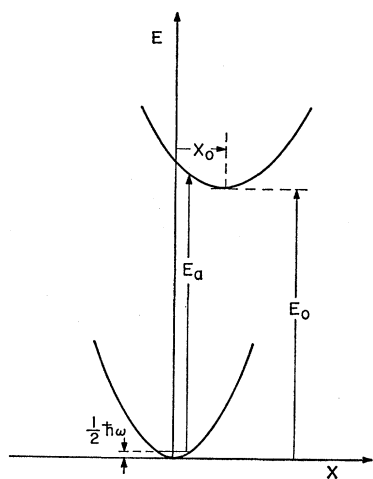


FIG. 1. Schematic configurational coordinate diagram of the system consisting of the F center and its six nearest alkali ions. The system energy E is plotted as a function of a coordinate X which collectively describes the positions of the nearest alkali ions. The lower parabola represents the ground electronic state of the system having force constant K , and the upper parabola represents the first excited electronic state with force constant K' . The minima of the parabolas are separated by E_0 in energy and X_0 in coordinate. At sufficiently low temperature only the lowest vibrational level of the ground electronic state is occupied. This level corresponds to the zero-point energy of the F -center system. This level has energy $\frac{1}{2}\hbar\omega$, where ω is the ground-state vibrational frequency influencing the center. The energy E_a is a typical electronic transition of the F center at low temperature from the lowest vibrational level of the ground electronic state to the first excited electronic state.

two different approximations, neither of which appear to be completely satisfactory. The first treats the lattice as a polarizable dielectric continuum in which the F center is embedded. This treatment has been employed by Huang and Rhys⁸ and Pekar,⁹ the latter having been the subject of a recent critical review by Fowler and Dexter.¹⁰ The second method, summarized by Klick and Schulman¹¹ emphasizes the interaction of the F center with its six neighboring cations, and employs a single configuration coordinate to describe the location of these ions with respect to the F center. This approach was first applied to the F center in several alkali halides by Russell and Klick,¹² and has been recently extended in studies by Lüty and Gebhardt¹³ and Klick, Patterson, and Knox.¹⁴ In general it is expected that the first treatment would have the greatest applicability in cases

⁸ K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

⁹ S. I. Pekar, Zh. Eksperim. i Teor. Fiz. **20**, 510 (1950); **22**, 641 (1952); Usp. Fiz. Nauk **50**, 197 (1953); and *Untersuchungen über die Elektronentheorie der Kristalle* (Akademische-Verlagsgesellschaft, Leipzig, 1954).

¹⁰ W. B. Fowler and D. L. Dexter, Phys. Stat. Sol. **2**, 821 (1962).

¹¹ C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

¹² G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

¹³ F. Lüty and W. Gebhardt, Z. Physik **169**, 475 (1962).

¹⁴ C. C. Klick, D. A. Patterson, and R. S. Knox, Phys. Rev. **133**, A1717 (1964).

where the F -center wave function is widely distributed around the center, while in the second, a well localized wave function would be preferable. According to both theoretical formulations the predicted temperature dependence of the half-width W of the F band is given by the same relation.¹⁰ If the F center in its ground state interacts with essentially one lattice mode of frequency ω , this relation for W as a function of the temperature T is

$$W(T) = W(0) [\coth(\hbar\omega/2kT)]^{1/2}, \quad (1)$$

where $W(0)$ is the half-width for T approaching absolute zero. This relation has been generally observed to agree reasonably well with experiment. The value of the frequency ω determined from such studies indicates that a vibration of lower frequency than the longitudinal optical mode of the lattice influences the center.^{5,14-16} This mode is likely a local vibration of the ions immediately surrounding the center.

The purpose of the present investigation is to study the effect of isotopic composition of the host lattice of an alkali halide on the F -center transition as observed in direct optical measurement of the F band. In general it would be expected that a series of perturbed F bands exist corresponding to various crystallographic arrangements of the naturally occurring isotopes at the lattice sites surrounding the F center. These differences could manifest themselves in the band shape as well as the spectral location of the band. Accordingly a fraction of the normal F bandwidth might be considered as arising from "isotopic broadening." The possibility of distinguishing particular isotopic influences on the F band would appear to be remote in crystals composed of elements in their natural abundances; however, characteristic differences of the F bands in isotopically enriched crystals might conceivably be observed.

The alkali halides which offer promise for such study are limited. In order that the maximum effect be obtained, it would appear desirable to study isotopic enrichments of the alkali ions, the nearest neighbors of the F center. The two isotopic forms of lithium, Li^6 and Li^7 , appear to offer the most likely possibility. The relative mass difference between these isotopes is about 1 part in 6. The choice of the anion to be used would not appear nearly as critical. The anions are second nearest neighbors of the F center and presumably would have considerably less influence on the electronic transition. Moreover, there are no halide isotopes of a given element with appreciable relative difference in mass. For practical reasons fluorine appears to be the most desirable halide for study in combination with lithium. The study of color centers in LiF has been greater than for other lithium halides, and the superior stability of LiF over the others to atmospheric moisture makes it

¹⁵ J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960).

¹⁶ J. J. Markham and J. D. Konitzer, J. Chem. Phys. **34**, 1936 (1961).

far more attractive for work involving sensitive optical absorption measurements. The predictions of theory can provide a judgement as to the anticipated differences in the *F* bands for the isotopic forms, Li⁶F and Li⁷F.

II. THEORY

The peak position and half-width are two parameters which would likely give indication of differences in the *F* band in Li⁶F and Li⁷F. We will use the configurational coordinate model in discussing these parameters. Figure 1 shows the usual configurational coordinate diagram of the *F* center in which the total energy *E* is plotted as a function of a coordinate *X*. *X* is the so-called configuration coordinate. This coordinate, for example, gives the radial displacement from equilibrium of the nuclei of the nearest alkali ions surrounding the vacancy, providing that the primary vibrational mode influencing the center is the symmetrical or so-called "breathing mode." For convenience *E*=0 is taken at the midpoint of the ground-state parabola, and *X*=0 corresponds to the usual ground-state interionic lattice distance. Electronic states are described by two parabolic curves with force constants *K* and *K'* for the ground and excited states, respectively. *E*₀ is the energy separation of the minima of the ground and excited curves, and *X*₀ is their coordinate separation. The vibrational levels of the ground state are separated by energy intervals corresponding to the ground vibrational frequency ω, the lowest or zero-point vibrational level having an energy ½ħω. A second frequency ω' can be considered to influence the center in the excited state.

a. Half-Width

Using the indices 6 and 7 to denote quantities associated with the two isotopic forms, Li⁶F and Li⁷F, respectively, the ratio of half-widths is obtained from Eq. (1),

$$\frac{W_6(T)}{W_7(T)} = \frac{W_6(0)}{W_7(0)} \left[\frac{\coth(\hbar\omega_6/2kT)}{\coth(\hbar\omega_7/2kT)} \right]^{1/2} \quad (2)$$

According to the configurational coordinate treatment, *W*(0), appearing in Eq. (1) is given as a function of *K*, *K'*, *X*₀, and ω,¹⁴

$$W(0) = 2(\ln 2)^{1/2} K' X_0 (\hbar\omega/K)^{1/2}. \quad (3)$$

The frequency ω is related to the force constant *K* and the mass *M* of the six nearest alkali ions of the *F* center,

$$\omega = (K/M)^{1/2}. \quad (4)$$

We take the point of view that the principal result of the alkali mass difference in the two LiF isotopes is a difference in the vibrational frequencies, and in turn a difference in the energies of the vibrational levels. Quantities which give the shapes and relative separations of the ground and excited state parabolas for the

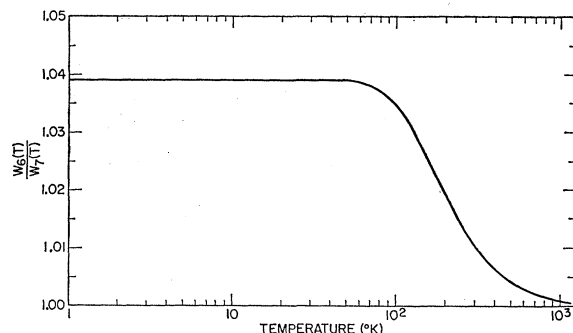


FIG. 2. Semilogarithmic plot of *W*₆(*T*)/*W*₇(*T*), the ratio of the *F*-band half-width in Li⁶F to the *F*-band half-width in Li⁷F, versus absolute temperature as given by Eq. (7). Values of ω₆ and ω₇ are taken from Eqs. (8) and (9).

F center, namely *K*, *K'*, *X*₀, and *E*₀ are taken to be nearly identical, so that essentially the same configurational coordinate diagram (exclusive of vibrational levels) may be considered to represent both *F* centers in Li⁶F and Li⁷F. It follows from Eq. (4), therefore, that the frequency ratio varies inversely as the square root of the alkali masses in the two isotopic forms,

$$\omega_6/\omega_7 \simeq (M_7/M_6)^{1/2} = 1.080, \quad (5)$$

giving a fourth root dependence for the low-temperature ratio of *F*-band half-width,

$$W_6(0)/W_7(0) \simeq (M_7/M_6)^{1/4} = 1.039. \quad (6)$$

Support for the above treatment comes from high pressure studies of the *F* band in alkali-halide crystals. These studies have not as yet yielded direct data on the parameters *K*, *K'*, *X*₀, and *E*₀ with pressure, however, the constancy of at least three of these quantities is implied by the fact that the *F*-band half-width is largely unaltered with an appreciable change in lattice constant in a number of alkali halide crystals.¹⁷ It is recalled from Eqs. (3) and (4) that the half-width is a function of *K*, *K'*, and *X*₀ for a given *F* center. For the two crystals here under consideration, Li⁶F and Li⁷F, there is a natural difference in the lattice constant of about 1 part in 5000, due presumably to the difference of zero-point energy of the two chemically equivalent lattices. The exact values of lattice constant determined by Thewlis¹⁸ using x-ray techniques are given in Table I. A fractional lattice constant difference of 1 part in 5000 in LiF would

TABLE I. Lattice constants of Li⁶F and Li⁷F at 25°C.^a

	Lattice constant (Å)
Li ⁶ F	4.0271 ± 0.0001
Li ⁷ F	4.0263 ± 0.0001

^a After Thewlis (Ref. 18).

¹⁷ I. S. Jacobs, Phys. Rev. **93**, 993 (1954).

¹⁸ J. Thewlis, Acta Cryst. **8**, 36 (1955).

result from the application of less than 400 atm of pressure. The findings of Jacobs¹⁷ for the F band in KCl, for example, indicate no appreciable change in half-width up to 5000 atm and a fractional change in lattice constant over 40 times as large as the above quoted fractional difference in lattice constant between Li⁶F and Li⁷F.

As indicated in Eq. (6) the half-width of the F band in Li⁶F is anticipated to be approximately 4% larger than the corresponding width in Li⁷F at sufficiently low temperature. The question arises as to the relative magnitudes of the F -band half-widths in the two isotopic forms at higher temperature. Upon substitution for the low-temperature half-width ratio, it follows from Eq. (2) that

$$W_6(T)/W_7(T) \simeq 1.039 [\coth(\hbar\omega_6/2kT)/\coth(\hbar\omega_7/2kT)]^{1/2}. \quad (7)$$

Values of ω_6 and ω_7 are not known and have not been obtained in this study by the usual continuous measurement of the temperature dependence of half-width. For purposes of Eq. (7) a reasonable estimate, however, for either of the frequencies can be obtained from Eq. (1) taking the average half-width data at only two temperatures. For ω_7 this value has been obtained from data determined in this study at room and liquid-helium temperatures,

$$\omega_7 = 2\pi \times 8.65 \times 10^{12} / \text{sec}, \quad (8)$$

and from Eq. (5) the value for ω_6 follows directly,

$$\omega_6 = 2\pi \times 9.34 \times 10^{12} / \text{sec}. \quad (9)$$

Figure 2 gives a semilog plot of the temperature dependence of the F -band half-width ratio, $W_6(T)/W_7(T)$, using Eq. (7) with values of ω_6 and ω_7 from Eqs. (8) and (9). It is clear that the maximum difference in half-width of the F bands in the two isotopic forms occurs at low temperature, and below about liquid-nitrogen temperature this difference is largely temperature-independent. Above liquid-nitrogen temperature the half-width ratio decreases and approaches unity. At room temperature the half-width difference would likely be below the level of experimental distinguishability with an anticipated difference of about 1%,

$$W_6(RT)/W_7(RT) \simeq 1.011. \quad (10)$$

b. Peak Position

Now let us consider a possible difference in peak position of the F band in the two isotopic forms of LiF. In this section the low-temperature behavior of the F -band peak position will be considered where only the lowest vibrational level of the ground electronic state is occupied. This level corresponds to the zero-point energy of the center. As indicated in Fig. 1, E_a is the energy necessary to raise the F center from this ground vibrational level to a point on the excited-state parabola

by a vertical or Franck-Condon transition. The final state is considered to be one of a classically continuous set of levels described by the excited-state parabola. This is reasonable in that the transition occurs to a point many vibrational levels above the minimum of the excited-state parabola.¹⁹ The analytic expression for E_a is given in terms of the parameters describing the configurational coordinate diagram,

$$E_a = E_0 + \frac{1}{2}(X - X_0)^2 K' - \frac{1}{2}\hbar\omega. \quad (11)$$

We designate these values of E_a for the two isotopic forms of LiF as E_a^6 and E_a^7 , and at the F -band maxima, $(E_a^6)_{\max}$ and $(E_a^7)_{\max}$. The difference in energy of the F -band maxima in the two LiF isotopes is thus given by

$$\Delta(E_a)_{\max} = (E_a^7)_{\max} - (E_a^6)_{\max}. \quad (12)$$

$\Delta(E_a)_{\max}$ can be thought of as arising from two small contributions in the two isotopes, first a difference in mass of the alkali ions, and second the accompanying difference in lattice constant. In this approximation

$$\Delta(E_a)_{\max} \simeq \left. \frac{\Delta(E_a)_{\max}}{\Delta a} \right|_{M \text{ const}} \times \Delta a + \left. \frac{\Delta(E_a)_{\max}}{\Delta M} \right|_{a \text{ const}} \times \Delta M, \quad (13)$$

where a and M refer to the lattice constant and the mass of the six alkali ions surrounding the F center, respectively.

From high-pressure data Jacobs¹⁷ has given the following relation between the frequency ν_{\max} , marking the F -band maximum and the lattice constant a ,

$$d(\ln \nu_{\max})/d(\ln a) = -n, \quad (14)$$

where the range in n for six NaCl-type alkali halides is small,

$$3.4 \leq n \leq 4.4. \quad (15)$$

Fitchen²⁰ has confirmed that Eq. (14) also holds reasonably well at low temperatures. Converting Eq. (14) to the present notation, $(E_a)_{\max} = \hbar\nu_{\max}$, we have

$$\left. \frac{\Delta(E_a)_{\max}}{\Delta a} \right|_{M \text{ const}} \times \Delta a \simeq -n(E_a)_{\max} \frac{\Delta a}{a}. \quad (16)$$

Taking $\Delta a/a \simeq -2 \times 10^{-4}$ from the data of Table I, and $(E_a)_{\max} \simeq 5$ eV for the F -band peak energy in LiF, it follows that approximate bounds can be placed on the first term on the right-hand side of Eq. (13),

$$0.003 \text{ eV} \leq \left. \frac{\Delta(E_a)_{\max}}{\Delta a} \right|_{M \text{ const}} \times \Delta a \leq 0.004 \text{ eV}. \quad (17)$$

An alternate approach in estimating the value given

¹⁹ F. E. Williams and M. H. Hebb, Phys. Rev. **84**, 1181 (1951).

²⁰ D. B. Fitchen, thesis, University of Illinois, 1962 (unpublished).

by Eq. (17) is to use the Mollwo relation for the F band in NaCl-type alkali halides in which the alkali mass again does not appear explicitly. Markham²¹ has given the following Mollwo relation for the F band based on liquid-helium temperature data taken from Rabin and Klick,²²

$$(E_a)_{\max} = 13.8(\frac{1}{2}a)^{-1.86}, \quad (18)$$

where $(E_a)_{\max}$ is given in units of electron volts and a in units of angstroms. It follows therefore that

$$\left. \frac{\Delta(E_a)_{\max}}{\Delta a} \right|_{M \text{ const}} \times \Delta a \simeq (-1.86)(E_a)_{\max} \frac{\Delta a}{a} = 0.002 \text{ eV}. \quad (19)$$

This estimate is in reasonable agreement with the determination of Eq. (17), and taking an average value from these expressions,

$$\left. \frac{\Delta(E_a)_{\max}}{\Delta a} \right|_{M \text{ const}} \times \Delta a \simeq 0.003 \text{ eV}. \quad (20)$$

The second term of Eq. (13) is the value of $\Delta(E_a)_{\max}$ under conditions where the lattice constant is unchanged and only the alkali mass difference is considered. This is precisely the approximation made above in evaluating the half-widths of the F band. In the absence of a lattice constant difference between Li⁶F and Li⁷F values of K , K' , X_0 , and E_0 are considered identical in the two crystals, and only ω_6 and ω_7 are assumed to differ in accord with the mass difference of the alkali ions, Li⁶ and Li⁷.

It is necessary first to obtain the value of X in Eq. (11) corresponding to the energy E_a at the peak position of the F band. Klick, Patterson, and Knox¹⁴ have given the expression for the probability of an absorption transition E_a as a function of X at low temperature as shown in Fig. 1,

$$P(X) = (1/K'(X - X_0))(K/\pi\hbar\omega)^{1/2} \times \exp(-KX^2/\hbar\omega). \quad (21)$$

The first factor in this expression, $1/K'(X - X_0)$, takes account of the finite curvature of the excited-state parabola over the range of values of X in which transitions E_a occur. If this range of values is small so that the corresponding portion of the excited-state curve is essentially linear, the first factor is independent of X . In this case the energy E_a corresponding to the F -band maximum occurs at $X=0$. Taking into account the curvature of the excited state, i.e., using the full expression given in Eq. (21) the band maximum is slightly displaced from $X=0$. This more precise value of X , obtained by setting the derivative of $P(X)$ with respect

to X equal to zero, is equal to

$$\frac{1}{2}X_0 - [(\frac{1}{2}X_0)^2 - (\hbar\omega/2K)]^{1/2}. \quad (22)$$

Upon substitution of this expression for X in Eq. (11) the value of the energy corresponding to the peak absorption is obtained as a function of the configurational coordinate parameters,

$$(E_a)_{\max} = E_0 + K'(\frac{1}{2}X_0)^2 + \frac{1}{2}K'X_0[(\frac{1}{2}X_0)^2 - (\hbar\omega/2K)]^{1/2} - \frac{1}{4}\hbar\omega(K'/K) - \frac{1}{2}\hbar\omega. \quad (23)$$

This expression can be put in a more simplified form taking

$$K \simeq K', \quad \text{and} \quad (\frac{1}{2}X_0)^4 \gg (\hbar\omega/2K)^2. \quad (24)$$

These approximations are based on determinations of the above quantities for KCl, KBr, KI, and NaCl.¹² It is presumed that similar approximations are valid for LiF. Applying Eq. (24) to Eq. (23), it follows that

$$(E_a)_{\max} \simeq E_0 + \frac{1}{2}K'X_0^2 - \hbar\omega. \quad (25)$$

The second term of Eq. (13) is directly obtained from the above expression for $(E_a)_{\max}$. If the lattice constant is held fixed for the two LiF crystals, K' , X_0 , and E_0 remain fixed as has been discussed, and only ω changes with the alkali-ion mass in the two isotopes. Hence

$$\left. \frac{\Delta(E_a)_{\max}}{\Delta M} \right|_{a \text{ const}} \times \Delta M \simeq \hbar(\omega_6 - \omega_7). \quad (26)$$

It is interesting that the magnitude of the above term is just twice the difference of the zero-point vibrational energies of the F centers in the two LiF isotopes, $\frac{1}{2}\hbar(\omega_6 - \omega_7)$. The additional contribution is attributable to taking account of the curvature of the excited-state parabola which acts to produce the additional shift of the F -band peak.

Upon substitution for ω_6 and ω_7 from Eqs. (8) and (9) into Eq. (26) it follows that

$$\left. \frac{\Delta(E_a)_{\max}}{\Delta M} \right|_{a \text{ const}} \times \Delta M \simeq 0.003 \text{ eV}, \quad (27)$$

One thus obtains for the combined difference in energy of the F -band maximum at low temperature,

$$\Delta(E_a)_{\max} = 0.006 \text{ eV}, \quad (28)$$

upon substituting Eqs. (20) and (27) into Eq. (13). The predicted peak position of the F band in Li⁷F is expected therefore to occur to slightly higher energy than the peak energy of the F band in Li⁶F. At the position of the F band in LiF this would amount approximately to only 3 Å.

A determination of the anticipated shift of the peak position of the F band in the two LiF crystals is considerably more difficult to estimate as the temperature is increased. The estimates for the first term on the right-hand side of Eq. (13) would follow similarly to the above treatment at low temperature, so that a value

²¹ J. J. Markham (to be published).

²² H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

TABLE II. Isotopic concentration of Li⁶ and Li⁷ in the LiF crystals studied.

Crystal	Source	Li ⁶ (%)	Li ⁷ (%)
Li ⁶ F	Harshaw	95.62	4.38
Li ⁷ F	Harshaw	0.09	99.91
Li ⁷ F	Argonne	0.03	99.97

given by Eq. (20) would be roughly expected. The second term of Eq. (13), however, becomes more difficult to evaluate with increasing temperature due to the occupancy of vibrational levels above the zero-point level of the ground electronic state. The difference in energy of these quantized states in the two LiF isotopes, $\hbar(\omega_6 - \omega_7)(n' + \frac{1}{2})$, increases with the quantum number n' . It is reasonable to expect, accordingly, that the shift in the peak position of the F band at increasing temperature will be at least as large as the value determined at low temperature as given in Eq. (27). Hence a combined shift of at least 0.006 eV would again be anticipated.

III. EXPERIMENTAL PROCEDURE AND RESULTS

Single crystals of Li⁶F and Li⁷F used in this study were obtained from the Harshaw Chemical Co. In addition a Li⁷F specimen was kindly supplied by Dr. D. Connor of the Argonne National Laboratory. These crystals were grown using isotopically enriched Li⁶ and Li⁷ with isotopic concentrations listed in Table II. Plates of thickness 0.10 to 0.12 mm were cleaved from these crystals for subsequent coloration and optical measurement. The purity of samples of these crystals was investigated by emission spectroscopy, and the results of the analysis are shown in Table III. It is seen that the impurity contents are reasonably identical for the indicated elements.

‡ Since it is well known that attempts to color LiF additively or electrolytically have been singularly un-

TABLE III. Spectroscopic analysis.^a

Element	Li ⁶ F (Harshaw)	Li ⁷ F (Harshaw)	Li ⁷ F (Argonne)
Li	VS	VS	VS
Na	VW	VW	FTR
K
Mn	TR	VW	...
Mg	FTR	FTR	FTR
Si	TR	VW	...
Fe	VW	TR	TR
Al	VW
Cu	FTR
Ca	FTR	VW	TR
Ba
Sr
Cs
Rb

^a The abbreviations and symbols used are as follows: VS—greater than 10%, S—1.0 to 10%, M—0.1 to 1%, W—0.01 to 0.1%, VW—0.001 to 0.01%, TR—0.0001 to 0.001%, FTR—less than 0.0001%, ...—not detected.

successful,²³ F centers were produced in this study by exposure to ionizing radiation. X rays were generated from a Machlett OEG-60 tungsten-target tube operated at 50 kV with a Bracke-Seib dc supply. The x rays were unfiltered except for passage through an approximate 1 mm beryllium entrance window to a Hofman liquid-helium Dewar. Irradiations and optical measurement at all temperatures were made within this Dewar which was provided with calcium fluoride windows for passage of the beam for optical measurement. Crystals were not exposed to room light throughout the course of these experiments once having been mounted within the Dewar. Optical measurements were made with a Cary, model 14M, spectrophotometer extending over the range of about 200–750 $m\mu$. In order to carry out the desired optical measurements with the greatest possible accuracy, the spectrophotometer used in this work was carefully adjusted for peak operation. The reproducibility, for example, of the spectral trace of the instrument over the above-mentioned spectral range was within the ultimate rating of the manufacturer, a magnitude of roughly the width of the line traced by the recording pen. This amounted to an optical density of approximately 0.002, and was maintained over several hours of operation, a period of time sufficient for the experimental measurement in this study.

In order to test the predictions of Sec. II above the F band was observed in both isotopic forms of LiF at liquid-helium temperature and room temperature. It was found that the most satisfactory technique for producing the F band was to perform the x-ray exposures at room temperature, and then to optically measure the resultant F band at room and liquid-helium temperatures. Irradiation of LiF at liquid-helium temperature was found to produce a broad, subsidiary band peaking near 350 $m\mu$, whose short wavelength tail strongly overlapped the F band. The F band produced at room temperature was free of this complicating structure. A small band appearing at about 450 $m\mu$, generally considered to be the M band, was observed as a result of the irradiations at room temperature. The peak optical density of this absorption was less than 2% of the peak optical density in the F band for irradiations carried out in this study.

In the present study two Li⁶F samples and two Li⁷F samples were employed. One of the Li⁷F samples was from the crystal obtained from the Argonne National Laboratory, and the remaining Li⁷F and the two Li⁶F samples were Harshaw specimens. The procedure adopted in measuring the F band in each of these specimens was the following. After cleaving and mounting the crystal in the low-temperature Dewar, a spectral base line for the unirradiated sample was established at room temperature. The crystal was cooled to liquid-helium temperature and a second base line was recorded. The crystal was then warmed to room temperature and

²³ P. Görlich, H. Karras, and G. Kötz, Phys. Stat. Sol. **3**, 1629 (1963).

a reconfirmation of the room-temperature base line was obtained. (The crystal was always given sufficient time to equilibrate upon a change in temperature.) The crystal was then colored with x rays at room temperature, and subsequently optically measured at room and low temperature. The x-ray exposures were chosen to produce colorations at the peak of the *F* band of optical densities of approximately 0.6 at room temperature. This coloration density allowed for a presentation of the optical-density data at both room and liquid-helium temperatures without a change in optical-density range of the spectrophotometer, avoiding a small but possible source of error in subsequent analysis of the data.

Figures 3 and 4 show data obtained at room temperature for one of the Li⁶F crystals, and at liquid-helium temperature for the Argonne Li⁷F crystal. The ordinate gives the change in optical density, $\Delta(\text{OD})$, obtained by subtracting the preirradiation base line from the spectrum after irradiation. Two facts are immediately evident from the data. First, a small band to the low-energy side of the *F* band is present at about 4.4 eV at liquid-helium temperature. As will be seen in subsequent data (Fig. 6) this band is present at liquid-helium temperature in Li⁶F also. The origin of this band is not known. The second observation to be made from Figs. 3 and 4 is that $\Delta(\text{OD})$ does not approach zero on the long and short wavelength sides of the *F* band. On the contrary an apparent underlying absorption is present which monotonically increases at higher photon energies. This type of behavior in coloration work is frequently attributed to scattering of the crystal not present prior to the irradiation. Whether or not such scattering is wholly or partially responsible for the apparent absorption, it is desirable to subtract this portion of the absorption change to obtain a more nearly "pure" *F* band. Unfortunately, this cannot be done with certainty; however, it can be done in a consistent manner in a given series of measurements. The method em-

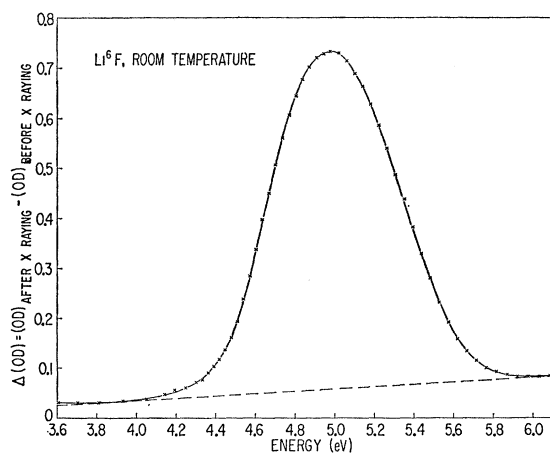


FIG. 3. The change in optical density produced by x raying a Li⁶F crystal as a function of photon energy. Both the irradiation and optical measurement were made at room temperature.

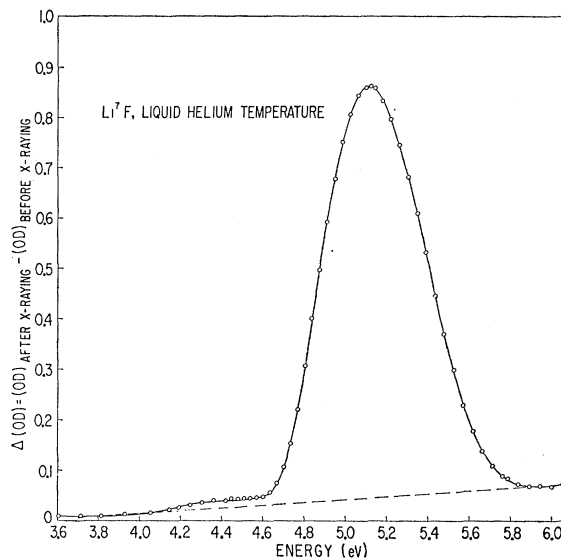


FIG. 4. The change in optical density produced by x raying a Li⁷F crystal as a function of photon energy. The irradiation was made at room temperature and the measurement was taken at liquid-helium temperature.

ployed here was to subtract points falling on the tangent to the lowest points on the long and short wavelength side of the *F* band, shown by the dashed lines of Figs. 3 and 4. The resultant values of $\Delta(\text{OD})$ were designated $\Delta(\text{OD})'$. Figures 5 and 6 show a summary of values of $\Delta(\text{OD})'$ normalized at the peak position of the *F* band for the four crystal specimens at room temperature and liquid-helium temperature, respectively.

The solid lines through the data points of Figs. 5 and 6 are sketched for the purpose of giving continuity to the points and indicating certain averages. The Li⁶F room-temperature data of Fig. 5 fall at slightly higher values than the Li⁷F data on the low-energy side of the *F* band. On the high-energy side of the band it appears that the data for Li⁶F and Li⁷F are fairly well intermeshed. The solid curve on the high-energy side of the peak of the *F* band in Fig. 5 is drawn to indicate that several of the Li⁷F points (plotted with the \square symbol) fall higher than the other three sets near the band maximum, and several of the Li⁶F points (plotted with the $+$ symbol) fall at slightly higher values than the other three near the tail. Data on the high-energy side of the peak of the *F* band at liquid-helium temperature, Fig. 6, show essentially the same behavior for corresponding crystals (plotted with the same symbols). The data on the low-energy side of the *F*-band maximum in Fig. 6, however, are clearly resolved for the two crystals. The points describing the Li⁶F data all fall at higher values than corresponding data for Li⁷F. Figure 7 shows an enlargement of the data in Fig. 6 in the vicinity of the half-maximum, indicating the clear difference of half-widths. It is worth mentioning that the same relative behavior between Li⁶F and Li⁷F as shown in Figs. 5 and 6 is

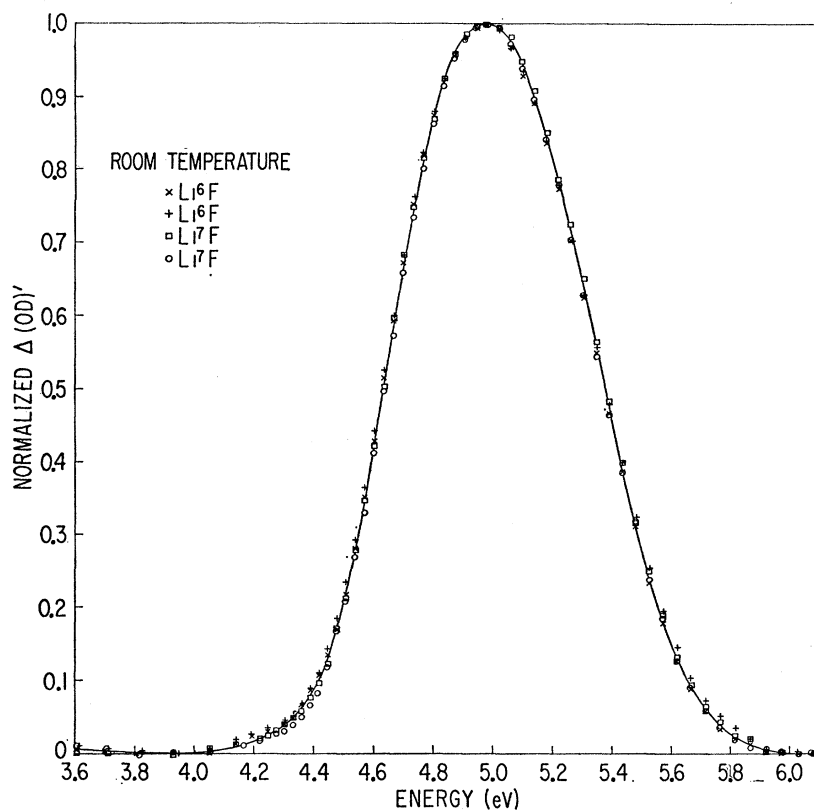


FIG. 5. Optical absorption spectra of the F bands in Li^6F and Li^7F . Values of $\Delta(\text{OD})'$ correspond to values of $\Delta(\text{OD})$ shown for one of the samples in Fig. 3 from which the points given by the dashed line are subtracted. Values of $\Delta(\text{OD})'$ for each F band are normalized to unity at the band maximum. Irradiations and optical measurements were performed at room temperature.

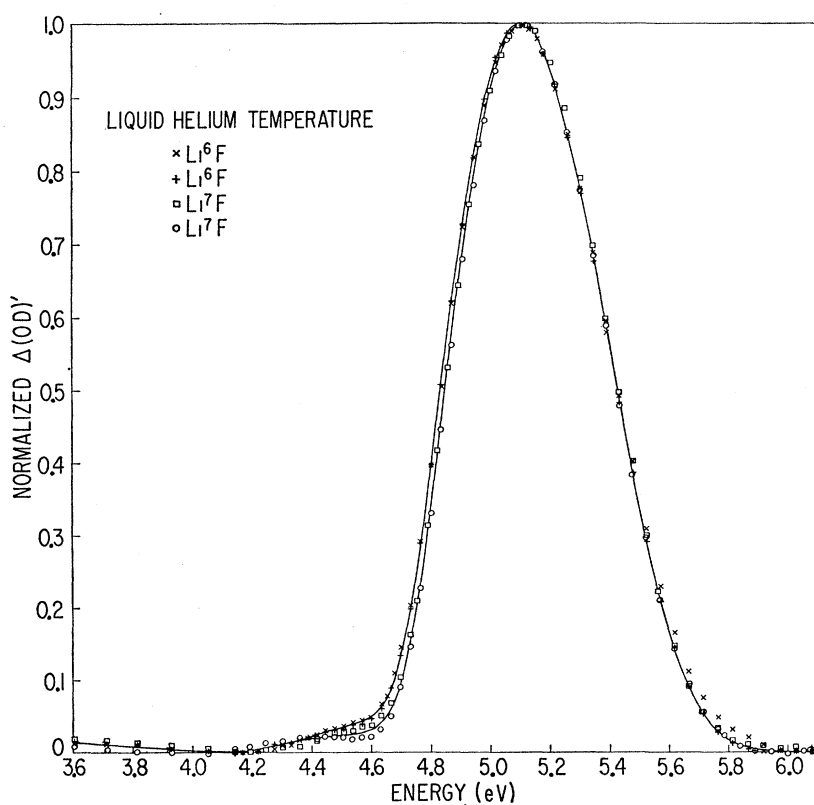


FIG. 6. Optical absorption spectra of the F bands in Li^6F and Li^7F . Values of $\Delta(\text{OD})'$ correspond to values of $\Delta(\text{OD})$ similar to those in Fig. 4 from which the points given by the dashed line are subtracted. Values of $\Delta(\text{OD})'$ which appear are normalized to unity at the peak of the F band. Irradiations were made at room temperature and optical measurements were performed at liquid-helium temperature.

TABLE IV. Experimentally determined values of half-width, W , and peak position, $(E_a)_{\max}$, for the F bands in Li^6F and Li^7F . All values are given in electron volts.

Temperature	Li^6F		Li^7F	
	$W_6(T)$	$(E_a^6)_{\max}$	$W_7(T)$	$(E_a^7)_{\max}$
Room temp.	0.743	4.968	0.748	4.977
	0.753	4.971	0.734 ^a	4.975 ^a
	Av. 0.748	4.970	0.741	4.976
Liq.-He temp.	0.598	5.103	0.584	5.115
	0.593	5.101	0.573 ^a	5.106 ^a
	Av. 0.596	5.102	0.579	5.111

^a Sample obtained from Argonne National Laboratory. All others from the Harshaw Chemical Corporation.

obtained by a direct normalization of $\Delta(\text{OD})$ data of Figs. 3 and 4. Accordingly, the relative behavior of Li^6F and Li^7F in Figs. 5 and 6 is substantially unrelated to the subtraction process described earlier in which values of $\Delta(\text{OD})$ were converted to $\Delta(\text{OD})'$.

A clear notion of the range of differences in the actual data points between Li^6F and Li^7F is provided in Fig. 8. The points of Fig. 8(a) are differences in the data of Fig. 5 in which values of $\Delta(\text{OD})'$ for Li^7F [denoted as $\Delta_7(\text{OD})'$] are subtracted from corresponding values of $\Delta(\text{OD})'$ for Li^6F [denoted as $\Delta_6(\text{OD})'$] for room-temperature measurements. The data of Fig. 8(b) are corresponding values taken from Fig. 6 at liquid-helium temperature. The solid curves shown in Fig. 8 are roughly sketched to indicate an approximate average of the plotted points. On the abscissa the positions of the F -band maximum, as well as the $\frac{1}{2}$ - and $\frac{1}{10}$ -maximum positions are shown.

Fixing one's attention on the liquid-helium temperature curve, Fig. 8(b) it is clear that the average difference reaches a maximum at about 4.8 eV. The average ordinate at this energy is over 5 times the average

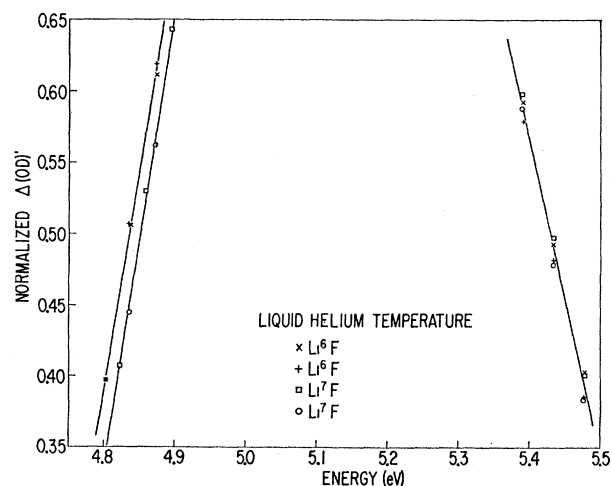


FIG. 7. Enlargement of data in the vicinity of the half-maximum for Li^6F and Li^7F given in Fig. 6.

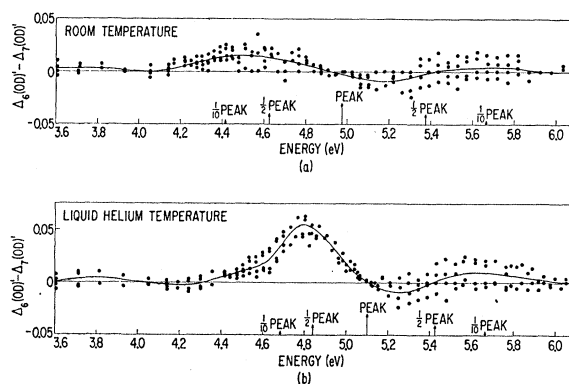


FIG. 8. (a) The difference in the normalized values of $\Delta(\text{OD})'$ shown in Fig. 5 for Li^6F and Li^7F x rayed and measured at room temperature. $\Delta_6(\text{OD})'$ refers to normalized values of $\Delta(\text{OD})'$ for Li^6F and $\Delta_7(\text{OD})'$ corresponds to normalized values of $\Delta(\text{OD})'$ for Li^7F . (b) The same differences for data shown in Fig. 6 for Li^6F and Li^7F x rayed at room temperature and measured at liquid-helium temperature.

fluctuation above and below the horizontal axis over the remainder of the spectrum. This arises from the difference between the Li^6F and Li^7F data on the short wavelength side of the F band, Fig. 6. The subsidiary absorption referred to earlier, falling on the low-energy side of the F band at about 4.4 eV at liquid-helium temperature would appear to be unrelated to the half-width difference which reaches a maximum near 4.8 eV. As was pointed out above in connection with Fig. 5 there appeared to be some slight amount of broadening of the F band in Li^6F on the basis of data on the low-energy side of the band. The difference curve of Fig. 8(a) indicates this to be the case. The average difference in the vicinity of 4.5 eV is somewhat larger than the averages over the remainder of the spectrum.

The results of values of half-width of the F band for the four samples whose data have been discussed are given in Table IV. These data were extracted from expanded plots such as given in Fig. 7. Also given in Table IV are corresponding peak positions of the F bands in the same crystals. The peak positions were extrapolated by successively halving the band widths in approaching the band maximum. This method of extrapolation was supported by the observation that the points marking the halved widths almost exactly followed a straight line. This technique appeared to be superior to the alternative method of linearly extrapolating the peak position from the absorption spectrum plotted on a semilogarithmic scale.¹² In the latter case the LiF data did not provide for a straight line extrapolation to the peak on a semilog plot owing to small but continuous curvature of the absorption data in approaching the peak.

IV. DISCUSSION AND CONCLUSIONS

Table V gives a comparison of the predictions and experimental values of the half-width ratio and peak-

TABLE V. Comparison of experimental and theoretical values of half-width ratio and peak-position difference for the F bands in Li^6F and Li^7F . The experimental quantities are determined from the average values given in Table IV, and the specified errors give the range of these quantities as determined from appropriate minimum and maximum values of Table IV.

Temperature	$W_6(T)/W_7(T)$		$\Delta(E_a)_{\text{max}}$ $= (E_{a^7})_{\text{max}} - (E_{a^6})_{\text{max}}$	
	Experiment	Theory	Experiment	Theory
Room temp.	1.009 ± 0.017	1.011 ^a	0.006 ± 0.003	≥ 0.006 eV
Liquid He-temp.	1.029 ± 0.015	1.039 ^b	0.009 ± 0.006	0.006 eV ^c

^a See Eq. (10) in text.

^b See Eq. (6) in text.

^c See Eq. (28) in text.

position difference of the F bands in Li^6F and Li^7F . The experimental values were computed from the average values of Table IV. The range of uncertainties are obtained by using appropriate combinations of the data of Table IV to yield the extreme values of the computed quantities. It is clear that a reasonable agreement between theory and experiment is obtained. The theoretical prediction of an enhanced F -band half-width for Li^6F , and the appearance of the Li^7F peak position at higher energy are experimentally observed. The magnitudes of the quantities both observed and estimated likewise are in approximate agreement. As was pointed out above, an anticipated half-width difference of about 1% at room temperature would not be experimentally observable. The uncertainty of the data between about 1 and 2% bears this out. This range of uncertainty, which also applies to the half-width ratio at liquid-helium temperature, places the observed value of about 3% sufficiently close to the predicted value of about 4%. The range of measured magnitudes of the shift in the peak position, falling between about 10^{-2} and 10^{-3} eV, are likewise within reach of the predicted magnitudes stated in Table V.

The uncertainty in the data do not allow for a determination as to whether the free ionic mass employed throughout this study should be replaced by an effective mass due to the coupling of the alkali ions to the rest of the lattice. Also, the percentage enrichments of the lithium isotopes used in this investigation, both in the high nineties, required only a small correction for comparison with theoretical values based on 100% enrichments. In accord with a much larger uncertainty in the data itself, this correction was not applied.

It should be pointed out as a subsidiary observation in this study that the F -band half-widths, Table IV, are

somewhat larger at low temperature than values previously reported.¹² Accordingly, the values of ω , Eqs. (8) and (9), are also larger than previous estimates. These enhanced values of ω now are in the neighborhood of roughly half the frequency for the longitudinal optical vibration of the LiF lattice, a result which seems to be more consistent with the F band in other alkali halides.¹²

A final word is in order on the possible presence of impurities that might impair the observation of an isotope effect on the F band. Needless to say this would be of concern in the instance where both isotopically enriched specimens contain either different impurities or different amounts of a given impurity. It is well known for example that slightly perturbed F bands can be produced when the F center associates with a neighboring alkali impurity. This center is called the F_A center. Several facts have emerged from studies of F_A centers^{24,25} that are worth mentioning in connection with the general problem of impurity effects in this study. First, the mere presence of the necessary impurity atom is not sufficient to insure the formation of an F_A center. Usually optical bleaching is required in a specific temperature range. Second, F_A -type bands are not known to occur when the radius of a foreign ion is larger than the ionic radius of the host alkali ion, e.g., F_A centers due to rubidium have not been observed in KCl and KBr , while both lithium and sodium are known to produce the centers in these salts. Thus, it would be expected in LiF , owing to the small radius of the lithium ion, a minimum number of possible substitutional impurities could lead to the formation of F_A -type centers in this lattice. These facts would tend to lessen the chance of possible complications arising from impurity perturbations on the F bands in LiF . The most reliable assurance for an isotope effect resides with the relative agreement of the experimentally observed F bands with the predictions of theory, and as we have seen in Table V this agreement is indicated for the F bands in the two isotopic forms of LiF studied.

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²⁵ K. Kojima, N. Nishimaki, and T. Kojima, *J. Phys. Soc. Japan* **18**, Suppl. II, 250 (1963).