

## Excited States of the $F$ Center in LiCl

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Excited states of the  $F$  center have been seen by Lüty in potassium and rubidium halides at energies up to several volts above the usual  $F$ -center transition. A molecular-orbital calculation of the  $F$  center in LiCl has been made by Wood, using only the  $2s$  and  $2p$  orbitals of lithium. From the levels thus computed, his tentative assignment of energies in eV to bands is 3.14( $F$ ), 3.92( $K$ ), 4.76–4.86( $L_1L_2$ ), and 6.14( $L_3$ ). Experiments are reported on LiCl colored by x rays at room temperature, cooled to 4°K, measured, bleached with incandescent light, and remeasured. The bleaching spectrum shows bands that are thought to be 2.14( $R_2$ ), 2.72( $R_1$ ), 3.30( $F$ ), 4.52( $L_1$ ), 4.95( $L_2$ ), 5.43( $L_3$ ), and 5.75( $L_4$ ). On the basis of the model of Klick and Kabler, which views the  $L$  bands as involving the excitation of the alkali to higher atomic states, the lithium atomic levels would have to be compressed by about 45% to agree with experiment. This amount of compression, which is larger than that for the salts previously measured, may be connected with the large dielectric constant of LiCl.

### INTRODUCTION

THE  $F$  center in alkali halides gives rise to a strong absorption band, called the  $F$  band, which has been extensively studied.<sup>1</sup> Lüty first showed that the  $F$  center also was the origin of several weak absorption<sup>2</sup> bands called  $L$  bands, at higher energy than the  $F$  band. This conclusion was further confirmed by the work of Hirai and Ueta<sup>3</sup> and Klick and Kabler.<sup>4</sup> These  $L$  bands are of special interest because they extend several volts above the  $F$  band and, from previous knowledge of the position of the  $F$ -center ground state in the energy band scheme, it is clear that the  $L$ -band transitions are to localized  $F$ -center levels with energies well within the conduction band.

The occurrence of such transitions has been somewhat surprising. It is not obvious, for instance, that impurity states within the conduction band would have sufficiently long lifetimes for normal optical transitions to occur. A second problem is conceptual. If the  $F$  center is viewed as a hydrogenic impurity, the series of excited bound states should end at the bottom of the conduction band. How, then, are states well within the conduction band formed?

Klick and Kabler<sup>4</sup> suggested a qualitative model for the origin of these higher excited states of the  $F$  center. It can be viewed most simply by considering the  $F$  band to arise from the transfer of the  $F$ -center electron to a neighboring alkali ion, which is thus converted to an atom. The higher excited states would then correspond to this same charge transfer with the resulting alkali atom simultaneously raised to one of its excited states. Reasonable agreement between the energy differences of the  $F$ -center states and isolated alkali atomic states are found for the potassium and rubidium salts if the

atomic levels are compressed 25 and 35%, respectively. This compression presumably arises from dielectric constant effects in the salt.

More recently Wood<sup>5</sup> has reported on a molecular orbital calculation of  $F$ -center energy levels in LiCl. The  $2s$  and  $2p$  Li orbitals were used and some contributions were included from ions as remote as the fifth nearest neighbors. Wood has assigned various of these  $F$ -center levels as levels between which the  $F$ -band,  $K$ -band, and  $L$ -band transitions are made.

No experimental data have existed for the excited states of the  $F$  center in LiCl and as a result it has not been possible to compare theory and experiment. The work described below was performed in an attempt to obtain information on the excited states of the  $F$  center in LiCl.

### EXPERIMENT

Commercial crystals of LiCl were used. Because this material is very hygroscopic, samples were cleaved and mounted on a helium Dewar inside a dry box flushed with dry nitrogen. The Dewar was evacuated for all measurements.

It was not possible to color the LiCl with x-rays at either 4 or 77°K. This is not surprising since the space available for an interstitial halogen atom is small; the magnitude of this space has been shown to be an important criterion for low temperature coloration.<sup>6</sup> The procedure used was to color LiCl with x rays at room temperature, cool to 4°K, bleach with tungsten light in the visible and near ultraviolet, and obtain the bleaching spectrum. Because of the surface stain which appeared at room temperature even with careful handling, the foregoing procedure produced spectra of higher resolution than the absorption spectrum itself. At 4°K the surface conditions stabilized and as a result the bleaching spectrum, obtained entirely at 4°K, could be taken with high accuracy.

Experimental results are shown for LiCl in Fig. 1. Optical density is plotted on the ordinate on a loga-

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<sup>1</sup> For a recent review of color centers see J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

<sup>2</sup> F. Lüty, *Z. Physik* **160**, 1 (1960).

<sup>3</sup> M. Hirai and M. Ueta, *J. Phys. Soc. Japan* **17**, 566 (1962).

<sup>4</sup> C. C. Klick and M. N. Kabler, *Phys. Rev.* **131**, 1075 (1963).

<sup>5</sup> R. F. Wood, *Phys. Rev. Letters* **11**, 202 (1963).

<sup>6</sup> H. Rabin and C. C. Klick, *Phys. Rev.* **117**, 1005 (1960).

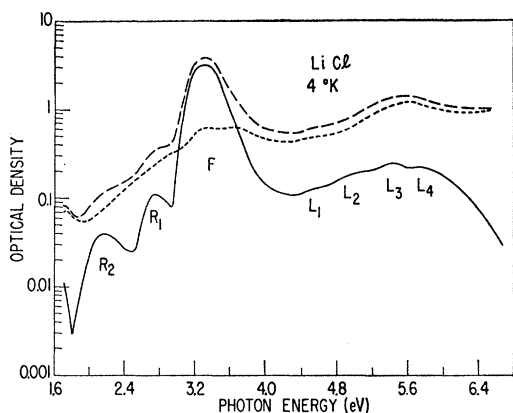


FIG. 1. Optical density of LiCl measured at 4°K. For a description of conditions, see the text.

rithmic scale for convenience. The upper dashed curve shows the measured absorption at 4°K of a crystal x-rayed at room temperature for 1 h at 50 kV and 20 mA. It shows several distinct peaks on a large background rising from the visible toward the ultraviolet. The crystal was next irradiated with white light for 5 min at 4°K. The glass envelope for the tungsten lamp excluded light of energy above about 3.8 eV. The resulting absorption spectrum, also measured at 4°K, is shown in the lower dashed curve of Fig. 1. It is seen that the principal absorption band is nearly completely bleached. The difference between these curves is a bleaching curve and is shown in the solid curve of Fig. 1. Letters for the various bands have been assigned by analogy with the more familiar alkali halides. The positions of the *F* band (3.30 eV), *R*<sub>1</sub> band (2.72 eV), and *R*<sub>2</sub> band (2.14 eV) are in reasonable agreement with previous experimental work and the predictions of these band positions using Ivey's relations.<sup>7</sup>

On the high-energy side of the *F* band is a broad band which may be a *V* band of some sort. Superimposed on the band is small structure which has been assigned to the *L* bands because of the similarity in position and intensity of these bands to the *L* bands in the potassium and rubidium salts. In Fig. 2 the *L* band region of the solid curve of Fig. 1 is shown in more detail. The ordinate scale is linear in optical density, and individual

TABLE I. Experimental and theoretical transition energies for the *F* center in LiCl.

Probable band	Energy of the absorption peak (eV)	Theoretical prediction <sup>a</sup> (eV)
<i>F</i>	3.30	3.14
<i>K</i>		3.92
<i>L</i> <sub>1</sub>	4.52	4.76-4.86
<i>L</i> <sub>2</sub>	4.95	
<i>L</i> <sub>3</sub>	5.43	6.14
<i>L</i> <sub>4</sub>	5.75	

<sup>a</sup> Reference 5.

<sup>7</sup> W. D. Compton and H. Rabin (to be published).

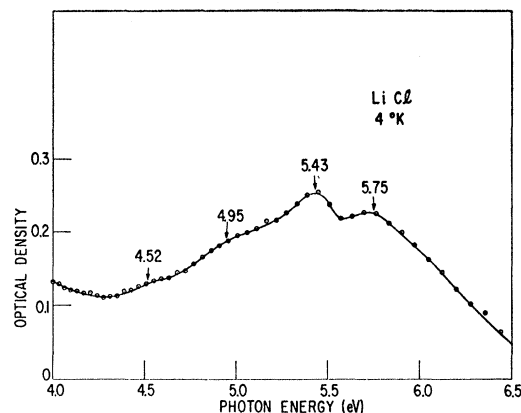


FIG. 2. A more detailed view of the *L*-band region of the bleaching curve for LiCl.

points are shown to give an indication of the measurement accuracy. From these data the following band assignments are made: *L*<sub>1</sub>(4.52 eV), *L*<sub>2</sub>(4.95 eV), *L*<sub>3</sub>(5.43 eV), and *L*<sub>4</sub>(5.75 eV).

These experimental band energies may be compared with those computed by Wood as shown in Table I. The computed energy of the *F* band is close to that observed experimentally. In the measurements it did not appear possible to see the *K* band. There is also reasonable agreement between the bands labeled *L*<sub>1</sub> and *L*<sub>2</sub> and the range of values computed theoretically. None of the experimental bands appears very close to the predicted position for the *L*<sub>3</sub> band.

Refinements of these calculations are being continued by Wood in an effort to eliminate some of the more troublesome approximations involved in the theoretical analysis.<sup>8</sup>

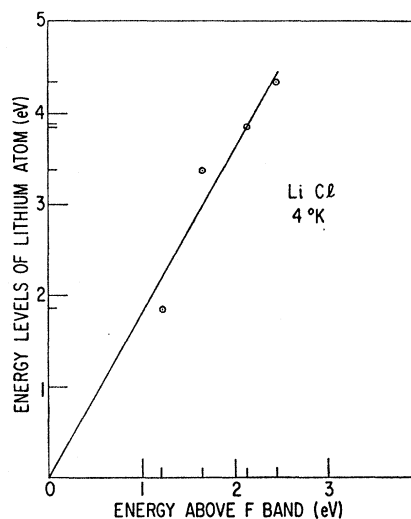


FIG. 3. On the ordinate are plotted the energy levels for atomic lithium. On the abscissa are plotted the differences in energy between the various *L* bands and the *F* band.

<sup>8</sup> R. F. Wood, Bull. Am. Phys. Soc. 9, 240 (1964).

These bands may also be compared with the model of Klick and Kabler by plotting the atomic energy levels of  $\text{Li}^0$  against the difference in energy between the various  $L$  bands and the  $F$  band. Such a plot, shown in Fig. 3, gives a reasonable straight line. The curve indicates that on the basis of this model, the atomic levels

of  $\text{Li}^0$  are compressed by about 45% in  $\text{LiCl}$ . This compression is larger than has been found for the potassium and rubidium salts. Since the compression is attributed to dielectric constant effects, a large value of compression would be expected for  $\text{LiCl}$  in view of its large dielectric constant.

## Temperature Dependence of the Ginzburg-Landau Coefficient in Type-I Superconductors\*

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Making use of surface superconductivity measurements, it is possible to obtain relatively precise values for the Ginzburg-Landau parameter  $\kappa$  as a function of temperature in certain type-I materials. We have measured the ac susceptibility to obtain  $H_{c3}$ , and the dc magnetization to obtain the bulk critical field, for Ta and three dilute alloys of Bi in Pb. The data are sufficiently accurate to distinguish between the various existing theories for  $\kappa$ ; the Ginzburg extension of the Ginzburg-Landau theory to low temperature predicts  $\kappa(t) = \kappa(0)_{G-L}(1+t^2)^{-1}$ , while Gorkov predicts  $\kappa(t) = \kappa(0)_G(1-0.24t^2+0.04t^4)$ , where  $t$  is the reduced temperature  $T/T_c$ . We find that the data fall on smooth curves which lie between the two theoretical predictions. Bardeen has used the two-fluid model to generate a temperature-dependent set of equations for the free energy, which yields the Ginzburg-Landau equations in the limit of  $t \rightarrow 1$ . Using the Bardeen two-fluid formulation, we find  $\kappa(t) = \kappa(0)_B(1+t^2)^{-1/2}$ . We find that the data fit the two-fluid temperature dependence more closely than they fit either the Gorkov or the Ginzburg relationship.

### I. INTRODUCTION

APPLICATION of the ac susceptibility technique<sup>1</sup> permits accurate experimental determination of the surface critical field  $H_{c3}$  in certain type-I and type-II superconductors. The theory of the surface critical field of Saint-James and de Gennes<sup>2</sup> relates  $H_{c3}$  to the Ginzburg-Landau<sup>3</sup> (G-L) parameter  $\kappa$  and to the thermodynamic critical field  $H_c$ . In this paper, we present experimental measurements on the temperature dependence of  $H_{c3}$  and  $H_c$  from which precise values for the temperature dependence of  $\kappa$  are obtained. These values are then compared with several theories which predict somewhat different temperature dependencies of the magnetic properties. In order to make a useful comparison of theory and experiment, it is important to clarify the terminology used for the parameters which determine the ratios of the upper critical fields  $H_{c2}$  and  $H_{c3}$  to  $H_c$ . A brief historical summary of the G-L,<sup>3</sup> Gorkov,<sup>4</sup> and Bardeen<sup>5</sup> theories,

and the pertinent parameters is presented followed by the experimental details, the results, and a comparison of the results with the theories.

### II. THEORY

The phenomenological equations of Ginzburg and Landau have given good descriptions of the behavior of London-type superconductors in magnetic fields. In particular, experiments have confirmed the Abrikosov<sup>6</sup> relationship between the bulk upper critical field  $H_{c2}$ , and the thermodynamic critical field  $H_c$  in type-II superconductors. Recently, Saint-James and de Gennes<sup>2</sup> have obtained a solution to the G-L equations, which show that in certain classes of superconductors (notably type II but including some type I) a superconducting region can nucleate in a surface layer at values of the applied external field appreciably greater than those sufficient to quench the bulk superconductivity. Their theory predicts a relationship between the surface critical field  $H_{c3}$  and the thermodynamic critical field  $H_c$ . The Saint-James-de Gennes relationship between  $H_{c3}$  and  $H_c$  has been confirmed in appropriate type I and type II superconductors.

Of central importance in both the G-L theory and in the Saint-James-de Gennes solutions is the linearized form of the equations and the fundamental parameter

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<sup>1</sup> M. Strongin, A. Paskin, D. G. Schweitzer, O. F. Kammerer, and P. P. Craig, *Phys. Rev. Letters* **10**, 442 (1964).

<sup>2</sup> D. Saint-James and P. G. de Gennes, *Phys. Letters* **7**, 306 (1963).

<sup>3</sup> V. L. Ginzburg and L. D. Landau, *Zh. Eksperim. i Teor. Fiz.* **20**, 1064 (1950).

<sup>4</sup> L. P. Gorkov, *Zh. Eksperim. i Teor. Fiz.* **37**, 833 (1959) [English transl.: *Soviet Phys.—JETP* **10**, 593 (1960)].

<sup>5</sup> J. Bardeen, *Phys. Rev.* **94**, 554 (1954); J. Bardeen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 274.

<sup>6</sup> A. A. Abrikosov, *Zh. Eksperim. i Teor. Fiz.* **32**, 1442 (1957) [English transl.: *Soviet Phys.—JETP* **5**, 1174 (1957)].