F-Band Oscillator Strength Determination in NaCl and KCl†*

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The *F*-band oscillator strengths in an x-irradiated NaCl crystal and an x-irradiated and an additively colored KCl crystal have been determined by a new method. The density of centers is determined by measuring the intensity of the paramagnetic resonance of the centers. Expressing the results in the usual way, using Smakula's equation, gives $f=0.87$ for NaCl and $f=0.85$ for KCl. Some of the assumptions involved in the use of Smakula's equation are criticized.

I. INTRODUCTION

THE most reliable oscillator strength determination for the *F*-band optical absorption has been that of Kleinschrod[1] for KCl. In that experiment the density of centers was measured by a chemical determination of the stoichiometric excess of alkali metal in additively colored crystals. This method assumes that all the excess metal is present as *F* centers. The trapping of electrons at more complex centers, the formation of a colloidal band, or the precipitation of excess metal at grain boundaries would introduce a serious error in the result. Criticisms of the chemical technique used are given by Scott.[2] Although the consistency of Kleinschrod's results for a range of a factor of ten in concentration suggests that his result is not in error, it seemed desirable to repeat the experiment by an independent method.

Further evidence for the value of the oscillator strength is given by the data of Pick[3] on the quantum efficiency of the optically induced $F\rightarrow F'$ transformation. This experiment, with the oscillator strength determined by Kleinschrod, gives the principal evidence for the accepted model of the F' center.[4] If the model is considered valid, however, the data then yield the *F*-band oscillator strength. This method assumes that the $F\rightarrow F'$ transformation is the only process induced by the absorption of light in the *F* band. If trapping of the photoelectrons at sites other than *F* centers is important, this experiment will give too low a value for the oscillator strength, and hence the method is open to some question. Further, a serious error in Kleinschrod's results would throw doubt on the model of the F' center and Pick's data would have to be reinterpreted.

In the present method, the density of centers is determined from the intensity of the paramagnetic resonance absorption of the *F* centers.[5,6] The presence of other centers, as long as all of the optical or paramagnetic absorption bands of these centers are distinct from those of the *F* band, does not affect the results of the experiment. This method, then, avoids some of the uncertainties inherent in the earlier determinations. Further, it is applicable to crystals in which it is impossible to avoid the formation of other bands and to crystals which have been colored by irradiation.

The intensity of the paramagnetic absorption is measured by a comparison with a known amount of a paramagnetic salt (the calibration salt). The oscillator strength, as usually expressed, is then obtained by comparing these results with optical absorption data and by using Smakula's equation.[7,8]

II. MICROWAVE EXPERIMENT—THEORETICAL

This section gives a theoretical justification of the procedure used in the microwave experiment. The details of the argument are presented more fully elsewhere.[9]

The microwave spectrometer gives a measure of the magnetic absorption, χ'', of a sample as a function of an applied magnetic field at a fixed microwave frequency. The problem is to determine the number of spins per unit volume, N, contributing to the observed χ''. The starting point for the argument is the Kramers-Kronig relation,[10]

$$\int_0^\infty \frac{\chi''(\nu)}{\nu}d\nu=\frac{\pi}{2}\chi_0, \tag{1}$$

and the usual expression for the static susceptibility of a system of spins,[11]

$$\chi_0=Ng_1{}^2\beta^2S(S+1)/3kT. \tag{2}$$

Here, $g_1{}^2$ is the diagonal element of the g^2 tensor in the

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[1] F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

[2] A. B. Scott, Nuovo cimento **1**, 104 (1955).

[3] H. Pick, Ann. Physik **31**, 365 (1938).

[4] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[5] Kip, Kittel, Levy, and Portis, Phys. Rev. **91**, 1066 (1953).

[6] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[7] A. Smakula, Z. Physik **59**, 603 (1930).

[8] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 663.

[9] R. H. Silsbee, thesis, Harvard University, 1956 (unpublished).

[10] J. H. Van Vleck, Massachusetts Institute of Technology Radiation Laboratory Report No. 735, 1945 (unpublished) and references quoted there.

[11] J. H. Van Vleck, *Theory of Electrical and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

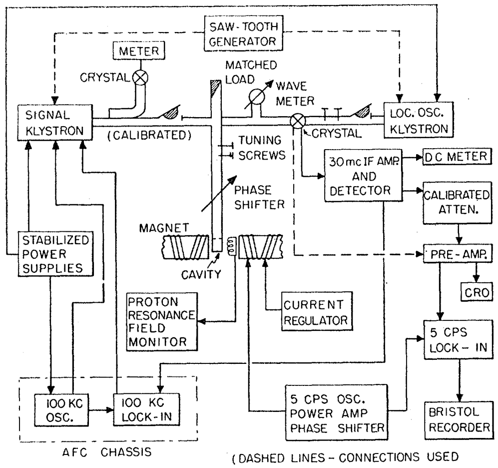

FIG. 1. Block diagram of microwave spectrometer.

direction of the oscillating field used in determining the χ'' of Eq. (1). The justification of Eq. (2), based both on the work of reference 11 and on arguments given by Pryce[12] concerning the use of the spin Hamiltonian formalism, will depend on the details of the energy level structure of the ion in question and on the magnitude of the interactions among the spins. Its validity must be considered for individual cases, especially at low temperatures.

These two equations will give N if χ'' is known for all frequencies. Since χ'' is measured as a function of applied magnetic field at a fixed frequency, Eq. (1) is not immediately applicable. It can be shown, however (see Appendix), that in many cases it is a good approximation to restrict the integration of Eq. (1) to a narrow region of the spectrum. In these cases the integral may be replaced by an integral over the magnetic field, giving

$$\int_{\text{resonance}} \chi''(H_0)dH_0 = N\frac{g_1^2}{g_0}\left(\frac{\pi h\nu\beta S(S+1)}{6kT}\right). \tag{3}$$

Here g_0^2 is the diagonal element of the g^2 tensor in the direction of the steady field, H_0.

Equation (3) gives the desired relation between χ'' and the spin density, N, and the discussion in the Appendix suggests some of the requirements for the validity of this extension of the Kramers-Kronig relation (1). There are two other practical considerations which limit the choice of the calibration salt. First, exchange narrowing or relaxation broadening of the line must not be important since the excessive contributions from the tails of a Lorentzian line make accurate integrations impossible. Secondly, since the resonance of the sample and the calibration salt are displayed on the same chart the g value and line width of the calibration salt must be chosen to allow satisfactory resolution of the observed signal into the contributions from the two paramagnetic species.

The salt chosen for this experiment was $\mathrm{CuCs_2(SO_4)_2 \cdot 6H_2O}$. Exchange narrowing is not important and the contribution of the relaxation width to the total width is only about 10%.[13] The principal source of the width is the hyperfine structure, the dipolar contribution being about 100 gauss for the orientation used in this experiment. The g factor shows a 15% anisotropy[14] and the crystal was oriented to give a g_0 with a large departure from 2. The F-center resonance is Gaussian in shape,[5] the width is due almost entirely to hyperfine interaction, and the g factor is isotropic. Curie's law [Eq. (2)] is well obeyed for both the copper salt and the F-center paramagnetism. Considering the assumptions outlined in the appendix, Eq. (3) should be accurate to within a few tenths of a percent for the copper salt, and to higher accuracy for the F centers. Since $S=\frac{1}{2}$ for both, Eq. (3) gives

$$\frac{N_F}{N_{\text{Cu}}} = \left(\frac{1}{g_0}\right)_F \left(\frac{g_1^2}{g_0}\right)_{\text{Cu}} \int \chi_F''dH \Big/ \int \chi_{\text{Cu}}''dH. \tag{4}$$

III. DETAILS OF MICROWAVE EXPERIMENT

A high-sensitivity microwave spectrometer,[15] illustrated in Fig. 1, was used to measure the relative values of χ''. The spectrometer, operating at 9000 Mc/sec, used a magic-tee bridge with a reflection cavity and superheterodyne detection. The field modulation and lock-in detection were at 5 cps. It was estimated that a room temperature measurement would give a signal-to-noise ratio of about 1 for a sample containing 2×10^{12} spins under the following conditions: resonance line width $=1$ gauss, microwave power level $=10$ mw, cavity $Q=5000$, and lock-in band width $=0.1$ cps.

Automatic frequency control is obtained by frequency modulation of the signal klystron. The microwave bridge circuit converts this to an amplitude modulation, the magnitude and phase of which depend on the balance condition of the bridge. A lock-in detector then gives the necessary correction voltage to the klystron reflector and keeps the frequency stabilized near the resonance frequency of the cavity. A particular advantage of this automatic frequency-control system is that it balances the bridge to give a pure absorption signal over a wide range of manual tuning. The dispersion signal may be obtained from the feedback circuit at the klystron reflector.

The output of the lock-in amplifier is approximately proportional to the derivative, $(d\chi''/dH)$, of the susceptibility with respect to the magnetic field, and the

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[12] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

[13] D. M. S. Bagguley and J. H. E. Griffiths, Proc. Phys. Soc. (London) **A65**, 594 (1952).

[14] Bleaney, Penrose, and Plumpton, Proc. Roy. Soc. (London) **198**, 406 (1949).

[15] R. H. Silsbee [Cruft Laboratory Technical Report No. 221, Harvard University, 1956 (unpublished)] gives a detailed description of the spectrometer.

integrated line intensity is given by

$$\int \chi''(H)dH = -\int (H-H_0)(d\chi''/dH)dH. \quad (5)$$

It can be shown[16] that the distortion of the line shape produced by using a large sweep amplitude does not affect the integrated line area. Distortions due to the lock-in response to harmonics of the lock-in frequency, or produced by the output time constant of the lock-in, again do not alter the integrated area.

Now, except for the filling factors of the calibration salt and the F centers, the sensitivity of the spectrometer to both samples will be the same. The cavity was a shorted piece of X-band wave guide coupled through an inductive iris and excited in a TE_{101} mode. The colored alkali halide crystal was placed at the end-plate of the cavity and filled the cavity to a depth of $\frac{1}{8}\lambda_g$(salt). The next $\frac{1}{8}\lambda_g$(salt) was filled with an uncolored crystal and the final $\frac{1}{4}\lambda_g$(air) was air. Small holes were cut in the alkali halide crystals to accommodate the calibration crystals. A calibration crystal was placed either at the center of the end plate of the cavity or at a quarter-wavelength from the end of the cavity in the center of the narrow wall of the cavity.

The relative filling factor for the two salts is easily computed, if one assumes the excitation of a pure TE_{101} mode. Estimates of the coupling to higher modes by the iris and by perturbations of the ideal cavity geometry suggest that the distortion of the field should be less than a few tenths of a percent. These estimates are not very reliable, however, and runs were made with the calibration crystal in both of the positions described above. These two positions have very different symmetry properties with respect to the cavity geometry, and different distortions of the field should be expected for the two types of runs. No systematic discrepancies were noted between these runs.

IV. OPTICAL EXPERIMENT

The optical experiment was conventional. A Perkin-Elmer Model 12C infrared spectrometer was used with quartz optics. The sample was placed in the exit beam of the instrument and the light detected with a 1P22 photomultiplier. Because of the large optical density of the crystals, a band-pass glass filter was used at the entrance slit of the instrument to avoid an excessive background from scattered light. The sample holder was designed so that an image of the spectrometer exit slit could be focused on the sample and the sample swept across this image. In this way an estimate of the homogeneity of the coloring could be obtained and an appropriate correction applied to the filling factor for the microwave experiment.

V. CRYSTALS

The x-irradiated NaCl and KCl crystals[17] were exposed for two and four hours respectively to a 150-peak-kev x-ray source operated at 5 ma. The distance to the anode was about 5 cm. To prevent excessive coloring at the surface by the soft component of the source and by secondaries, the crystals were sandwiched between plates of NaCl during the exposure. To improve the uniformity, the crystals were inverted after the first half of the exposure. The additively colored crystal[18] was prepared by a double oven technique. A rapid quench prevented the formation of R centers but there was evidence of a small concentration of M centers.

The crystals were worked to size on a damp cloth stretched over a glass plate. The grinding techniques originally used were found to produce serious distortion of the surface layer and bleaching to depths as great as 0.010 in. in both x-irradiated and additively colored crystals. The crystals were always handled in subdued red light, and optical measurements were made both before and after the microwave runs to be sure there had been no bleaching of the centers. The bleaching due to all causes during a run was always less than 2%.

The purity of the $CuCs_2(SO_4)_2 \cdot 6H_2O$ used for the calibration salt was estimated by the manufacturer[19] to be better than 99.5%. The crystals used in the experiment were grown from an aqueous solution of the salt. A chemical analysis[20] of several sets of crystals which came out of solution both near the beginning and the end of the evaporation gave the proper stoichiometry to within the 1% accuracy of the analysis.

VI. RESULTS

The final results are based on both microwave and optical data taken on the same crystals. Because of the danger of saturating the F-center resonance,[6] a series of four or five curves was taken in each microwave run, varying the power level near the onset of saturation. Two such curves are reproduced in Fig. 2. From these curves, the ratio of the areas of the F-center and calibration salt resonances can be determined to within a few percent, in the limit of no saturation. Additional curves were taken to determine the background signal due to impurities in the crystals.

The reproducibility between different runs was much poorer than the internal consistency of individual runs, the maximum discrepancy between runs on the same crystal being 10%. This is much larger than the estimated accuracy of the method and may be the result of imperfect reproducibility of the cavity geometry.

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[16] E. R. Andrew, Phys. Rev. **91**, 425 (1953).

[17] Obtained from Harshaw Chemical Company.

[18] This was a Harshaw crystal colored by Dr. J. J. Markham and Dr. G. Noble of Zenith Radio Corporation.

[19] A. D. McKay Chemical Company.

[20] Performed by Dr. S. M. Nagy of the Massachusetts Institute of Technology.

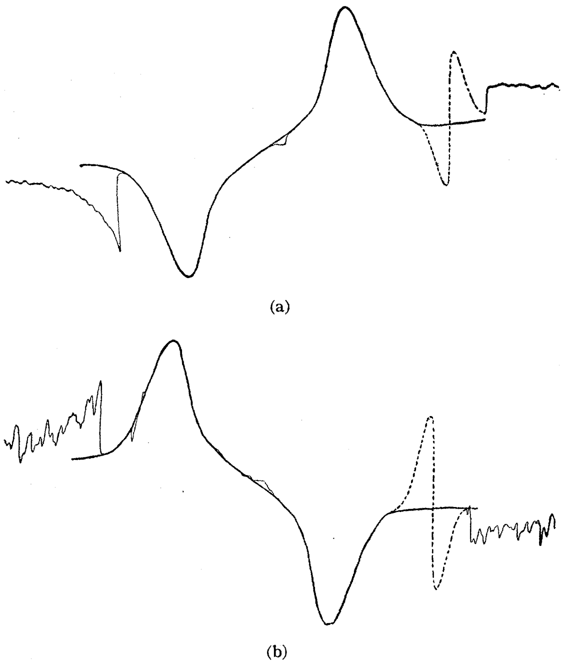

FIG. 2. Paramagnetic resonance data. (a) 30-db microwave attenuator; 20% F-center saturation. (b) 45-db microwave attenuator; no F-center saturation. The heavy solid line is the signal from 1.11 mg of $CuCs_2(SO_4)_2 \cdot 6H_2O$. The original recorder trace has been inked over. The dashed line is the F-center signal for crystal KCl No. 25M with a concentration of 1.3×10^{17} F-centers cm^{-3}. The original trace was removed during reproduction. The light trace at either end of the curve was taken at ten times the gain of the central portion to allow observation of the detail in the tails of the Cu^{++} resonance. The noise level at the high gain gives an indication of the signal-to-noise ratio.

The optical data, taken on the same crystals, were analyzed in two ways. First, the F-band absorption (after subtracting a correction for reflection and scattering from the surfaces) was fitted to a Lorentzian line-shape of the same height and width at half-maximum, and the oscillator strength determined from Smakula's equation. This has been the customary procedure in the past and the oscillator strengths so derived are directly comparable with those of other workers. Further, these oscillator strengths, together with Smakula's equations will give the correct F-center density in other crystals. There are serious objections to the use of Smakula's equation in comparison with theory, however, and these will be discussed in Sec. VII.

The results are also presented in a manner which does not involve Smakula's assumptions, namely, in terms of the integrated absorption cross section. In evaluating this cross section the area of the optical absorption was obtained in two ways. First the line was integrated numerically. A rather arbitrary subtraction is required on the short-wavelength side of the band to remove the contribution of the K-band absorption. The integrated area was also obtained by fitting the curves to a Gaussian form. The fit could be improved by using a skew Gaussian (see Figs. 3 and 4), but the area obtained did not differ significantly from that obtained from a simple Gaussian. Theoretical considerations of Lax[21] suggest that the spectral distribution function for the dipole matrix element should be nearly Gaussian. Since the observed absorption is proportional to the frequency times this dipole matrix element, a linear term (the term $x\sigma/\nu_0$ in Fig. 4) should be included. This term will have some effect on the center frequency of the absorption, but will not affect the integrated absorption significantly. The results for the line area determined numerically and by fitting to a Gaussian agreed to within several percent.

The inhomogeneity of the coloration in the long direction of the crystal, as determined by scanning the crystal in the optical experiment, was of the order of 15% in the worst crystal. A correction based on this scanning could be applied, and the error introduced in the f value by this inhomogeneity was estimated at less than a few percent. Inhomogeneities across the short dimension are averaged linearly in the microwave experiment and nearly so in the optical experiment, and no correction was applied. A 10% variation in homogeneity in this direction should give less than half a percent correction to the f value. Finally, microwave measurements using a geometry sensitive to variations in center density through the thickness of the crystals indicated that such inhomogeneities should introduce less than a 1% error.

The line shape of the paramagnetic resonance absorption for the F center, after the subtraction of a much broader background signal, was Gaussian to within the experimental error. The resonance absorption of other centers, if significant, would be expected to give an observable distortion of the line shape. The absence of such distortions suggests that the observed resonance was due to F centers alone. Further, the reasonable agreement between the results on an x-irradiated and an additively colored crystal for KCl indicates that the effects of hole centers are not important.

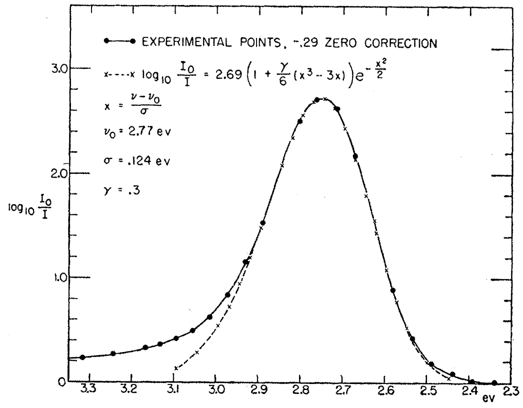

FIG. 3. Optical absorption of NaCl No. 8A at liquid nitrogen temperature.

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[21] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

The f values for NaCl are based on two microwave runs and two optical runs (one at liquid-air temperature) on a single x-irradiated crystal. For the KCl, data were taken on one additively colored and one x-irradiated crystal. A total of five microwave and three optical runs was analyzed for these crystals. In all three crystals, the F-center concentration was about 10^{17} cm^{-3}. Several different calibration crystals were used in the microwave experiment and about the same number of runs were made, with the salt, in each of the calibration positions. The estimated standard error for the values given for the oscillator strengths is 5%.

The final results are given in Table I together with the values obtained by Kleinschrod[1] and Pick.[3] The integrated cross section for F-band absorption is given as well as the oscillator strength derived on the basis of Smakula's equation.

The three results are in good agreement for KCl, and some confidence may be placed in using this oscillator strength in determining F-center concentrations from Smakula's equation. The agreement for NaCl is not satisfactory. Since it is difficult to prepare additively colored NaCl without the formation of complex centers or colloid, it is possible that Pick's results are in error. Trapping of photoelectrons at sites other than F centers in Pick's experiment would lead to a low value of f, and such a process in his experiment may be the cause of the discrepancy.

VII. SMAKULA'S EQUATION

The use of Smakula's equation has been questioned by several authors.[22,23] The first criticism is that the shape of the F-center absorption is more nearly Gaussian than Lorentzian, and the use of the Lorentzian fit in Smakula's equation overestimates the oscillator strength by a factor of about 1.5. Though an important correction, this presents no real problem in the interpretation of such an experiment.

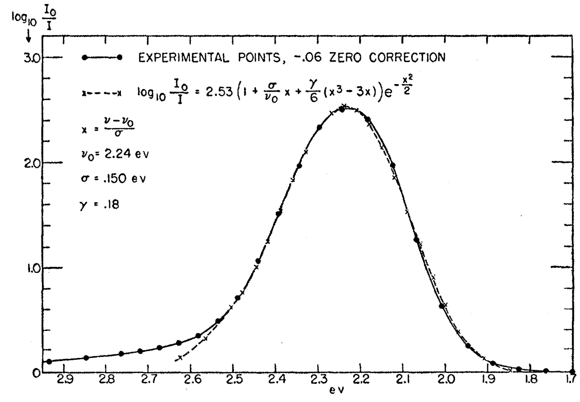

FIG. 4. Optical absorption of KCl No. 25M at room temperature.

TABLE I. Integrated absorption cross section and oscillator strengths for F band in KCl and NaCl.

Crystal	$(1/N)\int k(\nu)d\nu$	f	$f_{\text{Kleinschrod}}$	f_{Pick}
KCl	0.85×10^{-16} cm^2 ev	0.85	0.81	0.83
NaCl	0.91×10^{-16} cm^2 ev	0.87		0.7

Secondly, Smakula's use of the Lorentz local field for absorption by an impurity center is not justified and leads too large a value for the local field. The use of the Lorentz local field is valid only if the polarizability of the impurity is very nearly equal to that of a host atom. But this is clearly not the case near an impurity absorption band, and the nonuniform polarization of the host crystal produced by the impurity is important in considering the magnitude of the optical absorption.

A classical calculation of the absorption by a classical damped oscillator placed in a spherical cavity in a dielectric is straightforward,[9] using Onsager's[24] treatment of the local field problem. Such a calculation gives for the absorption constant

$$k(\nu)=\frac{\pi Ne^2}{mc}\left(\frac{9n^3}{(1+2n^2)^2}\right)\left(f\frac{\gamma/2\pi}{(\nu_0'-\nu)^2+(\gamma/2)^2}\right). \tag{6}$$

In this equation, n is the index of refraction of the host, f and ν_0 the oscillator strength and resonant frequency of the oscillator *in vacuo*, and γ is the damping constant. The maximum of the absorption is shifted from that of the free oscillator by the interaction with the host crystal and the new frequency is given by

$$\nu_0'=\nu_0-\left(\frac{2n^2-1}{2n^2+1}\right)\left(\frac{e^2f}{8\pi^2ma^2\nu_0}\right), \tag{7}$$

where a is the radius of the spherical cavity containing the oscillator. Equation (6) is essentially of the same form as Smakula's, but with a local field given by

$$E_{lO}=[3n^2/(2n^2+1)]E, \tag{8}$$

instead of the Lorentz field,

$$E_{lL}=\tfrac{1}{3}(n^2+2)E. \tag{9}$$

The ratio of the squares of these local field values is about 0.75 for NaCl, and the difference between the two values is clearly significant. The model is of course too idealized to have quantitative significance, but it does illustrate the inadequacy of the usual approach, and should give a better approximation than Smakula's equation.

If the crystal is considered as a lattice of classical oscillators, with only dipolar interaction, a detailed calculation of the absorption by an impurity (an oscillator of frequency different from that of the host)

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[22] D. L. Dexter, Phys. Rev. **101**, 48 (1956).

[23] C. Herring, in Proceedings of the Atlantic City Conference on Photoconductivity, Atlantic City, November, 1954 (to be published).

[24] L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

gives results qualitatively the same as above. Herring[25] has also given a very simple argument which leads to essentially the same conclusions.

These considerations may have some significance in the case of a well-localized impurity. For the case of the *F* center, however, the large extension of the *F*-center wave function over the nearest-neighbor shells makes the use of any local field picture extremely questionable. If a local-field concept is used, the average local field will be even less than that given by Eq. (8) and hence the error involved in the use of the Lorentz value for the local field is even worse. Secondly, the use of the dipole approximation in evaluating the transition probability for optical absorption is not valid because of the significant variation in the electric field over the center.

The most rigorous approach is that outlined by Dexter[22] in which the crystal as a whole is treated quantum-mechanically, and there is no need to introduce the local-field concept. To obtain any useful results the calculation had to be restricted to a localized impurity and a host lattice of low polarizability. Neither assumption is valid for *F* centers in the alkali halides. The calculation is carried only to first order in (n^2-1) and, to this order, is in agreement with both Smakula's equation and Eq. (6).

A possible approach to the problem would be to consider the *F* center and one or two nearest-neighbor shells as a quantum-mechanical system. If the energy levels and transition probabilities of such a system *in vacuo* could be calculated, then Eq. (6) might give a satisfactory means of correcting for the effects of the *F*-center interaction with the rest of the crystal.

VIII. CONCLUSIONS

A measurement, by an independent method, of the *F*-band oscillator strength in both an x-irradiated and an additively colored KCl crystal confirms the earlier values for this oscillator strength. The results of this work suggest a higher value for the oscillator strength of NaCl than that obtained by Pick. The method described should be applicable to many problems where chemical determinations of paramagnetic concentrations are not feasible, in particular to irradiated crystals.

IX. ACKNOWLEDGMENTS

The author wishes to thank Professor Harvey Brooks for suggesting this problem and for many discussions concerning the techniques of the experiment and the theoretical problems related to the *F*-band absorption. Dr. Karl Willenbrock first assembled and used the microwave spectrometer. His advice and comments concerning all aspects of the experiment were most welcome.

APPENDIX

The purpose of this appendix is to indicate under what conditions Eq. (3) may be expected to be valid.[26] The entire contribution to the integral of Eq. (1) will be from values of ν near the resonance condition,

$$h\nu=g\beta H_0, \tag{A.1}$$

if the spin selection rule $\Delta m=\pm 1$ is rigorously obeyed. This selection rule may be relaxed, however, by any interaction which does not commute with the Zeeman term in the Hamiltonian. This would include hyperfine and dipolar interactions, and, where $S>\frac{1}{2}$, crystalline field interactions. These same interactions also produce a broadening or splitting of the main resonance line, and the extent of the relaxation of the $\Delta m=\pm 1$ selection rule may be estimated, since it may be shown to be proportional to the square of the ratio of the broadening to the magnetic field at resonance.

For the particular case of dipolar broadening, the work of Van Vleck[27] shows that the relaxation of the selection rule reduces the contribution of the main line to the integral of Eq. (1) by an amount $\sim 2(H_d/H_0)^2$, where H_d is the contribution of the dipolar interaction to the line width. Further, if the hyperfine interaction is given by $A\mathbf{I}\cdot\mathbf{S}$, then the relative contribution of the forbidden transitions, for $S=\frac{1}{2}$, is $\frac{1}{3}(A/g\beta H_0)^2 I(I+1)$. The effect of crystalline field splittings for $S>\frac{1}{2}$ requires detailed consideration in individual cases.

Finally, in the case of an isotropic g value, the oscillating and steady magnetic fields must be mutually perpendicular to prevent absorption near zero frequency.[28] This requirement is changed if the g factor is anisotropic, and in this case the oscillating field must be perpendicular to the static magnetization of the spins rather than to the applied field. If this condition can not be satisfied—and it may prove impossible to do so with two nonequivalent ions in the unit cell—the observed χ'' is reduced by a factor

$$\left(1-\frac{(\mathbf{H}_0\cdot\mathbf{g}^4\cdot\mathbf{H}_0)}{g_1{}^2g_0{}^2H_0{}^2}\cos^2\beta\right). \tag{A.2}$$

Here β is the angle between the magnetization vector and the oscillating field. This correction could be neglected in the present experiment, but might become important for ions with highly anisotropic g values. Under these conditions, then, the integral in Eq. (1) may be restricted to the region near the resonance absorption. The integral in Eq. (1) must now be expressed in terms of an integral over magnetic field. The integral may be written as[27]

$$\int_{\text{resonance}}\frac{\chi''(\nu)}{\nu}d\nu=C\sum_{l,n}|(l|M_1|n)|^2, \tag{A.3}$$

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[25] See reference 23, Eqs. (14), (15), and (16). The assumption $|\alpha_C|\ll|\alpha_H|$ made by Herring in deriving Eq. (16) is not justified, and, as a result, the factor $(1-\zeta\alpha_H)$ of Eq. (16) should be squared. This result is then equivalent to Eq. (11) of the present paper if ζ is chosen appropriate to the classical model.

[26] See also the related discussion by R. T. Schumacher and C. P. Slichter [Phys. Rev. **101**, 58 (1956)].

[27] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[28] L. J. F. Broer, Physica **10**, 801 (1943).

where the summation is restricted to those pairs of states l, n for which $|E_l-E_n|\sim g\beta H_0$. M_1 is the magnetic-moment operator of the spin system in the direction of the oscillating field and C is a constant.

Now the matrix elements will be nonvanishing only for $|E_l-E_n|$ near the Zeeman energy and perhaps for satellite, partially forbidden lines. If the line is sufficiently narrow, there is no ambiguity about which pairs of states must be included in the summation, even if the values of the matrix elements are determined (from the measurement of χ'') by varying the magnetic field rather than the frequency. Then, if the moment matrix elements are independent of H_0, the summation may be expressed as an integral over H instead of one over frequency. Hence, for a narrow resonance, and if the moment matrix elements are independent of H_0, the introduction of suitable constants gives Eq. (3) of Sec. II. Now, the interactions already discussed, which relax the selection rule $\Delta m = \pm 1$, will also result in a field dependence of the value of the moment matrix elements. The correction to Eq. (3), however, is only of the order of the fourth power of the line width to the resonant field and may be neglected if the effect of the relaxation of the selection rule is itself unimportant.

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Fast-Neutron Damaging in Nuclear Reactors: Its Kinetics and the Carbon Atom Displacement Rate*†

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It is shown that the radiation damage produced in graphite at near room temperature is labile. A theory describing this lability is developed. Then using this theory and an identification and determination of the portion of the neutron flux spectrum responsible for the damage as obtained in another paper, the displacement rates for the condition that no annealing had intervened are calculated from the number of displacements which had been determined in graphite samples which had been irradiated near room temperature. From several different methods there is obtained, within a factor of 2, the following result: 10^{-21} displacements atom per damaging neutron/cm^2 for the number of displacements which remain after a scattering event involving a fast neutron near the beginning of the irradiation under conditions in which thermal annealing is not occurring.

I. INTRODUCTION

AFTER the discovery of large property changes in graphite subjected to fast-neutron bombardment,[1–3] attempts to determine the relationship between the neutron flux and the rate of displacement of carbon atoms (assumed to be the initiating cause of the property changes) were made by both theoretical calculations and experimental determinations. Among the former were the unpublished estimates of a rudimentary nature made by Wigner and others[4] and of a more detailed character made by Seitz and James. The theoretical problems are difficult because it is necessary to calculate the amount of energy dissipated in one of a number of possible ways in an energy range in which the dissipation is not amenable to exact theoretical calculation. Thus even the recent estimates by Seitz[5] and Snyder and Neufeld[6] differ by orders of magnitude, and the recent estimate by Harrison and Seitz[7] alter Seitz's estimate by a factor of 3. It is therefore desirable to establish an experimental value. Two such attempts (unpublished) were made in the early work, one by I. Estermann from stored energy data, and one by W. H. Zachariasen. Aside from the difficulties of relating the property changes which are observed to the number of displacements, these attempts to estimate the displacement rate suffered from lack of knowledge of the flux of neutrons which traversed the samples and from lack of knowledge of the fraction of originally displaced atoms no longer present in the samples. A similar criticism can be directed against more recent determinations by G. R. Hennig and J. D. McClelland (unpublished) and by Antal, Weiss, and Dienes.[8] In addition it may be mentioned that there has been a variability in property changes which were observed under various

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

† This paper together with several others (references 35, 9, 10, and 20) form a set on the subject of fast-neutron damaging in nuclear reactors.

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