

energy range and the peak at 12.25 eV arises from  $L_3 - L_3'$  transitions.

In conclusion the EPM calculation allows an identification of most of the optical structure in NaCl and confirms many of the assignments made by Roessler and Walker<sup>2</sup> who used the MgO band structure as a prototype. The theoretical  $\epsilon_2(\omega)$  gives the positions in energies and the shapes of the optical structure in agreement with experiment, but the magnitudes of the peaks are not in good agreement with experiment.

We would like to thank Professor W. C. Walker and Dr. D. M. Roessler for sending us their results prior to publication and for helpful discussions. A complete critical-point analysis and  $\epsilon_2(\omega)$  with constant matrix will be given in the forthcoming paper.

†Alfred P. Sloan Foundation Fellow.

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## LINEAR STARK EFFECT OF ELECTRO-OPTICALLY ALIGNED $F_A$ CENTERS\*

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Using selective optical excitation under high dc fields,  $F_A$  centers were aligned with respect to their optical-absorption tensors and microscopic inversion asymmetry. This ordering process removes the macroscopic inversion symmetry of the crystal, allowing the measurement of first-order electro-optical effects in the  $F_A$  absorption. The analysis of the linear Stark effect provides information about size and sign of the dipole-moment difference between ground and excited  $F_A$  states.

Many color centers consisting of a complex of two or more lattice site defects lack microscopic inversion symmetry. For the simplest case, two neighboring nonidentical point defects, the complex can be called a "defect dipole," with a vector indicating its orientation. The application of an electric field parallel to the defect dipole should produce a first-order change in the optical transitions of the defect because of the difference in electric dipole moment  $\Delta p$  of its ground and excited state.<sup>1</sup> For a macroscopic system of defect dipoles, however, this first-order effect cancels (for all absorption bands which are broad compared with the Stark shift) because of the existence of equal amounts of defect dipoles in opposite directions; only a much smaller second-order effect remains.<sup>1</sup>

We consider the  $F_A$  center [an  $F$  center with a (100) neighboring foreign cation] as the simplest example of a defect dipole with  $C_{4v}$  symmetry.<sup>2,3</sup> Partial alignment among the six equivalent defect-dipole states ( $x$ ), ( $\bar{x}$ ), ( $y$ ), ( $\bar{y}$ ), ( $z$ ), ( $\bar{z}$ ) can be achieved by irradiation with (100) polarized light, inducing for the selectively excited centers reor-

ientation jumps into one of the equivalent neighboring configurations [Fig. 1(a)]. This process achieves at most a full ordering of the absorption tensors ("optical alignment") with equal amounts of dipoles in opposite directions [e.g., the states  $x$  and  $\bar{x}$ ] in Fig. 1(a)].

The application of a dc electric field will produce a polarization of the center (particularly a displacement of the  $\text{Li}^+$  ion) which should remove the equality of reorientation jumps during optical alignment. As illustrated in Fig. 1(b) this may for instance increase the jump rate of process  $A$  and decrease that of process  $B$ , thus producing an excess of dipole states  $x$  vs  $\bar{x}$ . This electro-optically aligned defect-dipole system should therefore reveal a first-order Stark effect proportional to the population difference  $N(x) - N(\bar{x})$ .

This behavior has been verified for  $F_A$  centers in KCl:Li and KBr:Li (additively colored and optically  $F \rightarrow F_A$  converted). In the experiment we start with an optically aligned  $F_A$ -center system, the defect dipoles being in the  $y$  and  $\bar{y}$  states [Fig. 1(b)]. By a proper (100) polarized-light excitation, these centers are reoriented into the  $x$

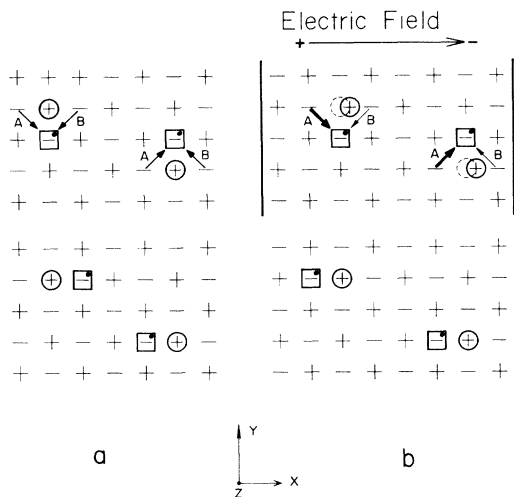


FIG. 1. Schematic representation of the optical reorientation process for  $F_A$  centers, originally in states  $y$  and  $\bar{y}$ . (a) Without field the jump rates  $A$  and  $B$  are equal (upper part), so that the same number of  $F_A$  centers in states  $x$  and  $\bar{x}$  are formed (lower part). (b) With applied dc field the jump rates  $A$  and  $B$  should be different. For the case, assumed here, that rate  $A > B$ , more  $F_A$  centers in state  $x$  are formed.

direction under a dc field applied in the  $x$  direction. The achievement of a population difference  $N(x) - N(\bar{x})$  is tested by a subsequent measurement of the field modulation of the  $F_A$  absorption by an ac field, applied in the  $x$  direction, using phase-sensitive photoelectric detection at the same frequency as the ac field. A strong signal is indeed observed, with magnitude proportional to the number of  $F_A$  centers which had been aligned under dc field into the  $x$  direction, and decreasing again in proportion to optical bleaching of these centers. This first-order Stark effect varies strictly linearly with the applied ac field up to  $10^5$  V/cm. Field modulation of the absorption constant  $\Delta K/K$  up to  $10^{-2}$  in KCl:Li and several times  $10^{-4}$  in KBr:Li have been achieved.

Figure 2 shows the spectral dependence of this first-order field-modulated absorption in KCl:Li. The observation of a strong effect in the  $F_{A1}$  band for  $x$ -polarized light and in the  $F_{A2}$  band for  $y$ -polarized light is in full agreement with geometry and transition vectors of the electro-optically aligned  $F_A$  centers. Moreover, the spectral shape follows closely a derivative  $dK/dE$  of the  $F_{A1}$  and  $F_{A2}$  bands, as expected for a rigid energy shift  $\Delta E$  of the bands by the ac field  $\Delta F$ :

$$\frac{\Delta K}{\Delta F}_{\text{obs}} = \eta \frac{dK}{dE} \frac{\Delta E}{\Delta F} = \eta \frac{dK}{dE} \Delta p.$$

Here  $K$  stands for the measured absorption of all  $F_A$  centers in  $x$  direction [i.e.,  $N(x) + N(\bar{x})$ ]. As the linear field modulation arises only from the difference  $N(x) - N(\bar{x})$ ,  $\eta$  has the meaning of an alignment ratio  $[N(x) - N(\bar{x})] / [N(x) + N(\bar{x})]$  produced by the dc-field reorientation. As detailed measurements have shown, this alignment ratio varies linearly with the applied reorientation dc field and increases considerably with decreasing temperature. At 4°K, where the highest defect dipole alignment can be achieved, a tendency for saturation of  $\eta$  is obtained at dc fields above  $6 \times 10^4$  V/cm. Assuming that this saturation behavior indicates full defect-dipole alignment ( $\eta = 1$ ), the difference in dipole moment  $\Delta p = \Delta E / \Delta F$  between ground and excited states of the  $F_A$  center can be obtained from the data. With a Lorentz correction for the applied field, we obtain  $\Delta p(F_{A1}) = 2.6 \times 10^{-9} e$  cm and  $\Delta p(F_{A2}) = 1.0 \times 10^{-9} e$  cm. As seen by the different sign of the two derivative curves in Fig. 2, the dipole moment changes  $\vec{\Delta p}$  for  $F_{A1}$  and  $F_{A2}$  transitions are opposite in direction.

For KBr:Li electro-optical alignment produces a field-modulated absorption, too, which again follows a derivative curve of the absorption (measured so far only in the  $F_{A1}$  band), but is smaller by 1-2 orders of magnitude. This large difference in size compared with the KCl:Li effect can arise either from a smaller value of  $\eta$  or of  $\Delta p$ . Moreover, the sign of the derivative curve, obtained after the same dc-field reorientation, is opposite that of the KCl:Li system.

A full interpretation of these results is only possible if one really knows whether the excess of the defect dipoles lies in the  $x$  or  $\bar{x}$  direction. This clearly depends on the specific way in which the dc field influences the reorientation process. KBr:Li and KCl:Li were chosen as examples for two completely different reorientation kinetics found among  $F_A$  centers ("type-I and type-II behavior").<sup>3</sup> An examination of the two different reorientation mechanisms involved<sup>4</sup> seems to predict an opposite field effect, which enhances process  $A$  vs  $B$  for  $F_A$  centers of type I [as indicated in Fig. 1(b)], but favors—under the same dc field—process  $B$  vs  $A$  for centers of type II. This could explain the observed opposite sign of the ac-field modulation for KCl:Li and KBr:Li. With this tentative assignment the  $F_{A1}$  band shifts to lower (and the  $F_{A2}$  band to higher) energies, if the electric field vector points from the  $\text{Li}^+$  to the vacancy. This in turn would mean that for the actual sign of our  $\vec{\Delta p}$ , in the  $F_{A1}$  transi-

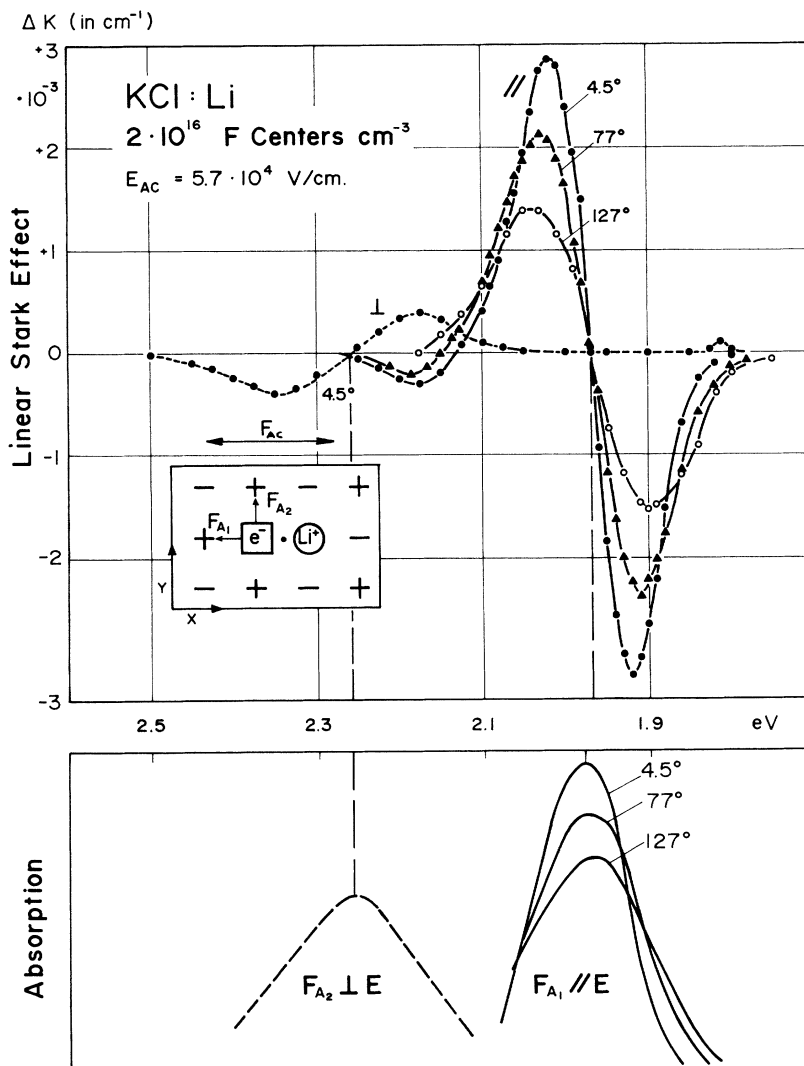


FIG. 2. Spectral dependence of the first-order field-modulated absorption of  $F_A$  centers (which were electro-optically aligned under a dc field of  $8 \times 10^4$  V/cm at 127°K) measured at three temperatures. The geometry of the aligned  $F_A$  center with its transition vectors and the direction of the applied ac field are indicated as well as the absorption spectrum and its polarization.

tion net electronic charge is moved toward the  $\text{Li}^+$  ion and in the  $F_{A2}$  transition, away from it. Considering predictions from ENDOR data<sup>5</sup> that the  $\text{Li}^+$  ion may be displaced from the vacancy, and in view of the very different charge distribution of the ground and the two excited states and their different overlap with the  $\text{Li}^+$  ion, this tentative result seems very reasonable.

An alternative interpretation of our results is possible if one assumes that the  $\text{Li}^+$  ion can be displaced from its normal position much more readily than normal lattice ions. The ac field would then modulate the  $\text{Li}^+$  ion distance from the vacancy, which could cause first-order shifts

of the energy levels of the ground and excited states. The difference of these shifts would show up as first-order Stark effect of the bands for aligned defect dipoles. This possibility is especially interesting in view of conclusions from recent Raman work<sup>6</sup> that the  $\text{Li}^+$  ion in the KCl  $F_A$  center may occupy off-center positions similar to the ones known for the isolated  $\text{Li}^+$  in KCl.<sup>7</sup> Detailed investigations on this question and all other aspects of this work are under way.

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### CRITICAL-FIELD MEASUREMENT OF SUPERCONDUCTING TUNGSTEN AS RELATED TO THE CERIUM-MAGNESIUM-NITRATE TEMPERATURE SCALE\*

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Measurements of the critical magnetic field curve of tungsten are presented and analyzed to determine the consequences of Abraham and Eckstein's proposed correction to the magnetic temperature scale for powdered cerium magnesium nitrate. The qualitative shape of the tungsten critical-field curve and the derived normal-state electronic specific-heat parameter  $\gamma$  favor a considerably smaller temperature correction than that suggested by Abraham and Eckstein.

Abraham and Eckstein<sup>1</sup> have recently reported new measurements of the heat capacity of powdered cerium magnesium nitrate (CMN) as a function of the magnetic temperature  $T^*$ . The powdered CMN sample itself, which had the shape of a right circular cylinder with diameter equal to height, served as the magnetic thermometer. Assuming that the measured heat capacity of powdered CMN is proportional to  $T^{-2}$  ( $T$  is the thermodynamic temperature) and also that CMN obeys a Curie law down to 6 mdeg K, Abraham and Eckstein conclude that for their thermometer  $T$  and  $T^*$  are related by the equation

$$T = T^* + \Delta \quad (1)$$

with  $\Delta = 1.7$  mdeg K. This choice for  $\Delta$  has an important qualitative effect<sup>1,2</sup> on the interpretation of experimental properties of pure liquid He<sup>3</sup> and of dilute solutions of He<sup>3</sup> in superfluid He<sup>4</sup>. In this Letter we examine the consequences of Eq. (1) upon the experimental critical magnetic field curve for superconducting tungsten. A complete discussion of the experimental details and results of the tungsten measurements will be deferred to a later publication.<sup>3</sup>

We have measured down to  $T^* = 2$  mdeg K the thermodynamic critical magnetic field  $H_c$  of a high-purity tungsten single crystal having resistance ratio 7500. It is important for the present discussion to note that the thermometer used in these measurements, consisting of CMN powder

packed into a right circular cylinder with diameter equal to height, was the same thermometer used in earlier experiments on pure He<sup>3</sup> in which both the heat capacity<sup>4</sup> and the attenuation of sound<sup>5</sup> were studied. The heat-capacity measurements<sup>4</sup> on He<sup>3</sup>, obtained by a difference method, also gave the cell background heat capacity which is presumably due to the CMN. This background heat capacity agrees with the CMN data used by Abraham and Eckstein to determine their relation between  $T^*$  and  $T$ . Therefore, if in our experiments the CMN thermometer and W sample were at the same temperature, the  $T^*-T$  relation proposed by Abraham and Eckstein for the heat-capacity measurements of CMN and of liquid He<sup>3</sup> must also apply to the W critical-field results.

Figure 1 shows the low-temperature portion of the critical-field data, plotted as  $H_c^2$  vs  $T^2$ , for two different runs made on the same W sample. The good quality of the data is indicated by the relatively small scatter within and between the two demagnetization runs. To facilitate making the correct extrapolation to  $T = 0$  (in order to obtain  $H_0$ , the critical field at  $T = 0$ ) we have used the thermodynamic relation between  $H_c^2$  and  $T^2$ ,

$$\frac{d(H_c^2)}{d(T^2)} = \frac{4\pi}{mT} [S_s(T) - S_n(T)], \quad (2)$$

where  $S_s$  and  $S_n$  are the molar entropies of the superconducting and normal states, respectively,