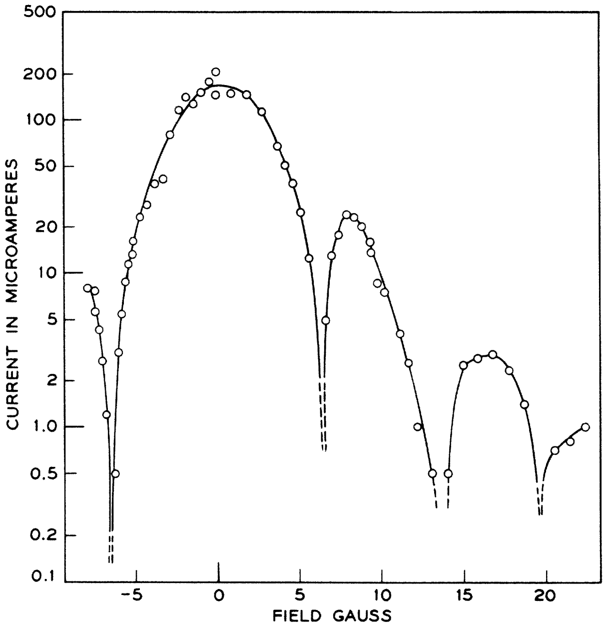

FIG. 3. The field dependence of the Josephson current in a Pb-I-Pb junction at 1.3°K.

ly decreasing maxima between. The area of junction containing flux is the width $W \times 2\lambda = 3.1 \times 10^{-8}$ cm^2 (see cross section of junction, Fig. 2). Thus a field of 6.5 gauss corresponds to a flux of 2.0×10^{-7} gauss cm^2 in the junction, which is indeed the flux unit. Considering screening and demagnetizing effects of the films, it is surprising that such a good value is obtained. A larger junction, 0.24×0.24 mm, had a period of 1.1 gauss, but the minima were not so well defined as the current did not reduce so effectively to zero. Again this corresponds to one flux unit being in the junction. For the large-area junction, 2.4×0.24 mm, the minima were poorly defined with approximately a 0.4-gauss period. If the full width of the junction is effective in carrying current, one obtains the flux as 7.5×10^{-7} gauss cm^2, but if $2\sqrt{2}\lambda_J$ is effective then the flux is 1.9×10^{-7} gauss cm^2. This appears to confirm the conclusion above that the Josephson current flow is confined to a width $2\sqrt{2}\lambda_J$ at the edge of the junction.

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$$J_1 = \tfrac{1}{2}\pi R_N^{-1}\Delta(T)\tanh\tfrac{1}{2}\beta\Delta(T),$$

but for Pb-I-Pb at 1.3°K this correction is negligible.

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EXCITED STATES OF THE *F*-CENTER ELECTRON

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In the past few years, interest in the excited states of the *F* center has been stimulated by the discovery of the *L* bands by Luty[1] and by the work of Swank and Brown[2] on the lifetime of the excited level responsible for the emission band of the center. Luty has attributed the *L* bands to excited levels lying above the *K* and *F* levels, and Swank and Brown have pointed out that their long-lifetime (~10^{-6} sec) results could be understood if an excited state existed, of the same symmetry as that of the ground state, lying just below the *F* excited level. The *K* band has long been attributed to an excited level of the *F* center.

Some time ago the present author[3] carried out calculations on the electronic structure of the *F* center in LiCl using the LCAO method in which the wave functions of the ground and excited states were expressed as linear combinations of the 24 2*s* and 2*p* orbitals on the six nearest-neighbor lithium ions of the Cl$^-$ vacancy. More in general, the wave function can be written as

$$\Psi_F(r) = \sum_{g,\mu} a_{g\mu}\varphi_{g,\mu}(\vec{r}-\vec{R}_g),$$

where $\varphi_{g,\mu}$ is the μth atomic orbital centered at the *g*th lattice site. The Hamiltonian of the *F* electron was taken as

$$H = -\tfrac{1}{2}\nabla^2 + \sum_{g=1}^{N} V(\vec{r}-\vec{R}_g).$$

The potential, $V(\vec{r}-\vec{R}_g)$, was taken to be that of a point ion except where it was possible to use a relationship such as

$$h\varphi_{g,\mu} = \epsilon_\mu \varphi_{g,\mu},$$

in which *h* is the Hamiltonian appropriate to the lithium atom. In such cases, ϵ_μ was taken to be the experimental ionization energy.

The solution of the usual secular determinant problem gave a level of Γ_1^+ symmetry (of the octahedral group) at about -5.1 eV and one level of Γ_4^- symmetry at about -2.1 eV. Optical transitions are allowed between these two levels and evidently account for the main *F* band. The next lowest level of Γ_4^- symmetry lay at +2.3 —much too far away to account for the *K* band. There was another level of Γ_1^+ symmetry at +0.6 eV and one of Γ_5^+ symmetry at +0.2 eV, and it was realized at the time that these states, in a more accurate calculation, might be lower and that they might possibly serve as electron traps.

These calculations have now been extended to include the 2*s* and 2*p* Li orbitals on the third-nearest-neighbor ions, the 2*s* orbitals on the fifth-nearest-neighbor ions, and, in the case of Γ_4^-, a 2*p* function located at the center of the vacancy. The results for the Γ_1^+, Γ_4^-, and Γ_5^+ irreducible representations are shown in Table I.

Before discussing these results, we shall give here a few comments on their reliability. Among other things, a great deal of the exchange of the *F* electron with the neighboring ions, the finite size of the Cl$^-$ ions, and, in part, the finite size of the Li$^+$ ions have been neglected. The three-center integrals which occur have not been calculated exactly. Experience has shown that these approximations will not greatly affect the transition energies if they are applied consistently in the ground and excited states. Of great importance, however, is the choice of a set of basis functions which must be large enough to allow flexibility in the rather extended excited-state wave functions. In these calculations, $E_1(\Gamma_1^+)$ and $E_1(\Gamma_4^-)$ are quite stable against extension of the basis set to include orbitals on more distant neighbors; $E_2(\Gamma_1^+)$, $E_2(\Gamma_4^-)$, and $E_1(\Gamma_5^+)$ have almost become stable. The other levels are still changing somewhat.

The multiplication table of the octahedral group shows that, starting from the ground-state level of Γ_1^+ symmetry, optical dipole transitions are allowed only to levels of Γ_4^- symmetry in the rigid, undistorted lattice. However, if it is assumed that, in the real crystal, some mechanism operates to make transitions allowed which would be forbidden in the rigid lattice, then it is possible to obtain good qualitative and even fairly good quantitative agreement with the experimental results. In Table I we have indicated the levels to be associated, tentatively, with each band, by a letter. All transitions go from the ground state lying at -5.77 eV.

Conway et al.[4] have shown, by a perturbation calculation, that, in the case of a Ag$^+$ ion in an alkali-halide crystal, zero-point vibrations can cause transitions between levels which would be forbidden in the free Ag$^+$ ion. Their arguments can be carried over, with very little modification, to our present problem and, indeed, the mechanism should be even more favorable here due to the relatively close spacing of some of the unperturbed levels shown in Table I.

Assuming that the zero-point vibrations can

Table I. Energy levels going with the various irreducible representations. The letters following some of the numbers are explained in the text.

Irreducible representation	Energy levels in electron volts E_1	E_2	E_3	E_4	E_5
Γ_1^+	-5.77 (*G*)	-1.85 (*K*)	+2.46	+7.46	+64.50
Γ_4^-	-2.63 (*F*)	-1.01 (L_1,L_2)	+0.37 (L_3)	+1.30	+5.84
Γ_5^-	-0.91 (L_1,L_2)	+1.00			

play the necessary role, the following interpretations are suggested. The origin of the *F* band is clear, although the agreement with the experimental result (3.12 eV) is probably fortuitous. In the real crystal, the zero-point vibrations will mix a small fraction of the wave function associated here with the *K* level with that associated with the *F* level and conversely. This will have the effects of making transitions to the *K* level partially allowed and of slightly increasing the lifetime of the *F* level. We feel that this may explain Swank and Brown's results on the temperature dependence of the lifetime of the excited *F* state at low temperatures. We do not believe that it is the explanation of the long lifetime of this level, which we attribute to the large Stokes shift and the necessity of modifying the usual, free-atom expressions for the radiative lifetime, as discussed by Fowler and Dexter.[5] In this connection, we point out that Pekar and Perlin,[6] using their continuum model, have obtained almost complete agreement with experiment. Because the *K* level is essentially of the same symmetry as the ground-state level, it seems at least plausible that the two will behave in a similar manner with temperature. Luty's result that the *K* band is temperature insensitive would then be understandable. In the absence of the zero-point vibrations, the L_1 and L_2 levels evidently lie close together. The perturbation then produces a large admixing of the wave functions going with these two levels of different symmetry. This might then be connected with Luty's rather peculiar results on the temperature dependence of the L_1 and L_2 bands. Finally, the excited level which is, presumably, responsible for the L_3 band is almost entirely of Γ_4^- symmetry in the real crystal with, perhaps, a small admixture of Γ_5^+ symmetry, and hence its temperature behavior should be similar to that of the *F* band, as Luty observed.

I wish to thank H. Schweinler for many helpful discussions, and R. Silsbee for bringing reference 4 to my attention.

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ADDITIVE COLOR CENTERS IN CALCIUM FLUORIDE

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Two sharp lines have been observed in the absorption spectrum of additively colored crystals of synthetic CaF_2 at 4.2°K. These lines have air wavelengths of 8434.1 and 8433.0 Å with the corresponding wave numbers 11 853.5 and 11 855.0 cm^{-1}. They are well resolved with an optical linewidth of about 0.3 cm^{-1}. This is believed to be the first time such sharp lines have been found in a color center spectrum. Although these lines were first observed in crystals with rare-earth dopants obtained from Semi-Elements, Inc., it has been found possible to produce the violet crystals containing the absorption lines by following the procedure of Bontinck.[1] CaF_2 crystals were heated in Ca vapor for two hours at 700°C in a sealed evacuated Vycor tube. Since no attempt was made to prevent optical bleaching, the general features of the spectrum are similar to those observed by Bontinck after irradiation with visible radiation. The color centers can be removed by heating in an evacuated system for one hour or less at 800°C.

The absorption spectrum shows large splitting under a uniaxial stress, similar to those previously observed for divalent samarium[2] and europium[3] in CaF_2. However, in this case the Zeeman spectrum depends on the direction of the applied magnetic field relative to the crystal axes, indicating that the centers have less than cubic symmetry. The longitudinal Zeeman spectrum is similar to the transverse spectrum with