but not at 6890 Å.

The relative intensity of scattered radiation as a function of wavelength is plotted in Fig. 2, where the vertical bars represent the standard deviation for the 10 experimental values. It is readily seen that satellites occur at about ±38 Å. The experimental point at ±23 Å is purposely omitted because the argon line at 6965 Å saturates the photomultiplier making it impossible to obtain a signal.

We attempted a least-squares fit of the theoretical curves to our experimental points but were unable to obtain a good fit because the observed linewidth is much wider than that predicted by the theory. The discrepancy may be accounted for by a variation of temperature in the plasma we observe. According to Ahlborn,[8] the temperature changes from 13 500 to 11 500°K in a distance of 1 mm. This leads to a decrease in electron density of one-half, if we assume local thermal equilibrium, and a spread of peak frequencies of the satellites of about 12 Å. This agrees very well with the width of the line observed.

If we use Ahlborn's value of 13 500°K for the temperature of the center of the plasma jet and estimate α (defined in Ref. 6) to be 4.4, we obtain a theoretical curve whose peaks coincide with the experimental peaks as shown in Fig. 2. This value of α leads to an electron density of 6.3×10^{16} cm^{-3}, in good agreement with the assumption of local thermal equilibrium.

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MODULATED F-CENTER ABSORPTION IN KCl

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The possibility of existence of higher excited states of the F center at energies corresponding to those of the conduction band has recently stimulated a great deal of theoretical investigation.[1-4] The occurrence of localized states of relatively long lifetime into a continuum of levels raises, in fact, a number of problems for the theory of solids.[5] The suggestion that optical transitions to higher excited states from the fundamental level of the F center were responsible for the absorption of the L bands in alkali halides was made by Lüty[6] on the basis of proportionality among L, K, and F bands. However, the proportionality between the F and K bands has been at times doubted,[7] and the ratio between the height of F and L bands in crystals x rayed at low temperature is only approximately equal to that found in additively colored crystals.[8] Doubts have also been raised in connection with the controversial value of the yield for photoionization into the L bands, and a different model for the L and the K "centers" has even been suggested.[9-11]

In this Letter we present direct experimental evidence that the L and K absorption bands in KCl are caused by transitions starting from the fundamental state of the F center. The results are obtained by use of a method of "modulated optical absorption" which is capable of being applied to other problems of current research in the field of color centers.

The principle of the method is the following: A crystal of additively colored KCl is exposed, at low temperature, to an intense beam of F light whose intensity varies with time at a frequency ν_0. As a result of this excitation, both the population of the ground state (F^0) and that of the first excited state (F^*) of the F center vary around their average value at the same frequency. An auxiliary orthogonal beam of continuous light, which passes through the crystal inducing transitions from the F^0 and the F^* levels, then shows amplitude modulation of frequency ν_0, which can be detected with great sensitivity[12] by use of synchronous amplifiers. Transitions starting from the F^0 level cause modulation in phase with the exciting F light; possible transitions from the F^* level would cause, in contrast, out-of-phase modulation. The method bears some resemblance with that used by Frölich and Mahr to study, with pulsed laser techniques, exciton absorption near an excited F center.[13]

The modulation index $\Delta I/I$ of the dc auxiliary light is shown in Fig. 1 as a function of energy, for a crystal of additively colored KCl ($N_F = 1.4\times10^{17}$ cm^{-3}) at liquid-nitrogen temperature. The exciting F light, chopped at 75 cps, has an intensity $I_{0F} = 5.4\times10^{16}$ photons sec^{-1}.

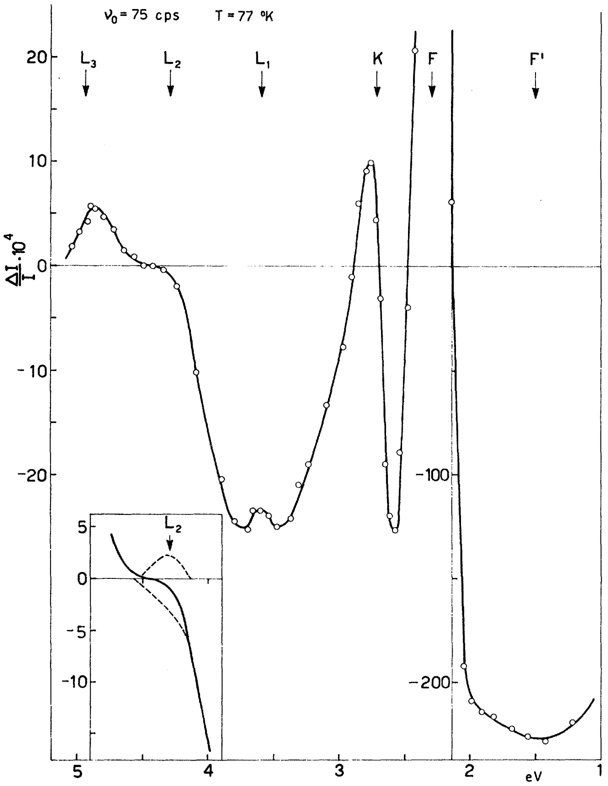

FIG. 1. Modulation index $\Delta I/I$ as a function of the energy of the photons for a crystal of KCl containing 1.4×10^{17} F centers/cm^3. In the insert the L_2 band is resolved.

Modulation shown as positive in the figure corresponds to a signal in phase with the exciting F light (the crystal becomes more transparent under F-light illumination). Positive peaks at energies corresponding to F, K, L_1. and L_3 bands are clearly visible. The L_2 peak is hidden under a much stronger negative signal, from which it can be resolved, as is shown in the insert of Fig. 1. A large negative peak at energies corresponding to the F' band is also present. The shape of the curve on the high-energy side of the F band is due to the superposition of F, K, F', and L signals with appropriate phases.

The results of Fig. 1 prove beyond reasonable doubts that the optical transitions giving rise to the K and L bands originate from the F^0 level and thus that the "K and L levels" are indeed higher excited states of the F center.

On the other hand, Fig. 1 shows that under the action of the F light at liquid-nitrogen temperature an unstable F' band is developed, which reconverts to the F band in the dark in times not much longer than $1/\nu_0$. Modulation corresponding to the formation of F' center is negative, as it should be.

The process can be represented by the double reaction

$$F^* + F \rightarrow F' + \text{vacancy} \tag{1}$$

followed by

$$F' + \text{vacancy} \rightarrow 2F. \tag{2}$$

It has been pointed out by Lüty[14] that processes (1) and (2) seem to involve the tunneling of an electron from the excited F^* level to a neighboring F center followed by field ionization of the F' center.

If $1/\tau_1$ and $1/\tau_2$ are the transition probabilities of Reactions (1) and (2) and $1/\tau_F$ the probability of the luminescent de-excitation of the F^* level, it can be shown, by solving the rate equations for the populations of the F^*, F', and F^0 levels, that the modulation index to be expected for transitions $F^0 \rightarrow F^*$ is[15]

$$M_F(\lambda, \omega) = \frac{2c}{a} I_{0F} \tau^* \left[1 + \frac{(\tau_2/\tau_1)^2 + 2\tau_2/\tau_1}{1+\omega^2\tau_2^{\,2}}\right]^{1/2}$$

$$\times [1 - \exp(-k_{F^0} a)] \Delta_F(\lambda), \tag{3}$$

where $\omega = 2\pi\nu_0$ is the chopping frequency of the exciting F light, c and a are the dimensions of the crystal in the directions of the measur-

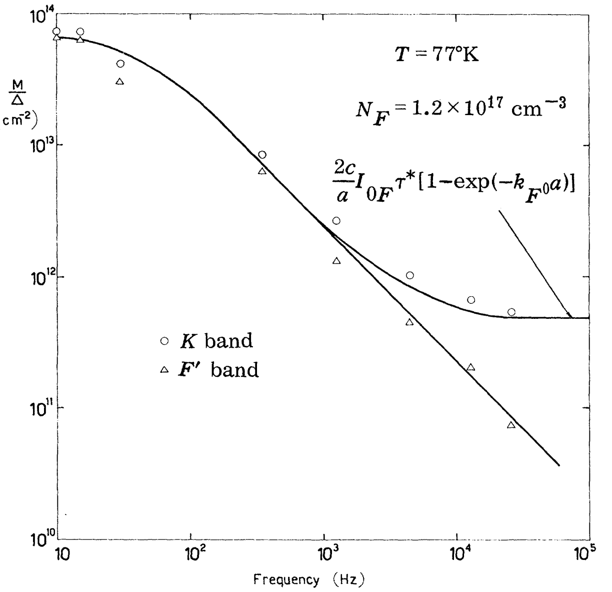

FIG. 2. Experimental values of M/Δ for the K and the F' bands as a function of frequency of chopping ν_0. The solid-line curves are obtained from Eqs. (3) and (4) (with $\tau_1 = 3\times 10^{-5}$ sec, $\tau_2 = 4\times 10^{-3}$ sec).

ing and the exciting light, respectively; τ^* is defined as $1/\tau^* = 1/\tau_1 + 1/\tau_F$, $K_F{}^0$ is the absorption coefficient at the wavelength of the excitation, while $\Delta_F(\lambda)$ is related to the absorption coefficient $k_F(\lambda)$ at the various wavelengths by

$$k_F(\lambda) = N_F \Delta_F(\lambda),$$

where N_F is the number of F centers per cubic centimeter. The modulation indexes for the transitions $F^0 \rightarrow K$ and $F^0 \rightarrow L_{1,2,3}$ have the same form (3) with the appropriate values of $\Delta(\lambda)$.

On the other hand, the modulation caused by transitions starting from the metastable F' level is given by

$$M_{F'}(\lambda,\omega) = \frac{2c}{a} I_{0F}\tau^* \frac{\tau_2}{\tau_1} \frac{1}{(1+\omega^2\tau_2{}^2)^{1/2}} \times [1-\exp(-k_{F^0}a)]\Delta_{F'}(\lambda). \tag{4}$$

In case $\tau_1 \gg \tau_2$, M_F/Δ_F and $M_{F'}/\Delta_{F'}$ coincide at low frequencies of chopping, i.e., the population of the F^0 level is, in such a case, mainly controlled by Reactions (1) and (2). At high frequencies, on the other hand, $M_{F'}/\Delta_{F'}$ goes to zero while M_F/Δ_F reaches the constant value

$$\frac{M_F}{\Delta_F} = \frac{2c}{a} I_{0F}\tau^*[1-\exp(-k_{F^0}a)], \tag{5}$$

the population of the F^0 level being governed by the rate of the luminescent de-excitation of the F^* level.

The experimental results at various frequencies for the F' and the K bands are compared in Fig. 2 with the curves obtained from (3) and (4) assuming $\tau_1 = 3\times 10^{-5}$ sec, $\tau_2 = 4\times 10^{-3}$ sec.[16] The agreement seems very satisfactory, especially if one considers that the limiting value of M_K/Δ_K for high frequencies contains only known or measured quantities (independent of the choice of τ_1 and τ_2, when $\tau_1 \gg \tau_F$). The value of τ_1 obtained from the results of Fig. 2 is approximately 50 times larger than τ_F. This shows that an electron excited to the F^* level has a 2% probability of decaying according to processes (1) and (2) (at liquid-nitrogen temperature in a crystal of KCl containing 1.2×10^{17} F centers/cm^3). Though the fraction of electrons decaying in this way is rather small, it is felt that the occurrence of Reactions (1) and (2) could explain the concentration quenching of the F-center luminescence.[17]

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DENSITY OF STATES AND THE LOW-TEMPERATURE SPECIFIC HEAT IN DILUTE MAGNETIC ALLOYS*

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Dilute magnetic impurities in noble metals exhibit a large excess low-temperature specific heat,[1] ΔC_v, compared to that of the pure host material. At very low temperatures ΔC_v is proportional to the temperature and is independent of the impurity concentration. Several models have been proposed to explain the anomalous low-temperature specific heat. In one proposed by Kondo[2] (henceforth to be denoted as model I), ΔC_v arises from an enhanced density of states which results from an effective internal field at the impurity site. The effective field, H, is given by the well-known Ruderman-Kittel[3]-Yosida[4] (RKY) interaction. Another model (to be denoted model II) was proposed by Marshall[5] and Klein and Brout.[6,7] Here, the excess specific heat arises from the magnetic disordering of those impurities which experience small effective internal fields, H. H arises again from the RKY potential.[8] The major difficulty with model II is the justification of the Ising model used.

The low-temperature magnetic specific heat is calculated relatively easily in an Ising model,[5-7] where it is found that ΔC_v is proportional to T and is independent of the concentration, in agreement with experiment. One can also calculate ΔC_v in a completely classical model,[9] where the effective field is a classical vector quantity. Here, ΔC_v is presumably proportional to T^3. This T^3 dependence arises because the effective field H is a vector quantity; and the probability $P(H)$ of having a magnitude of H between H and $H+\Delta H$ is $P(H) = 4\pi H^2 P(H_I) dH$. $P(H_I)$ is the probability distribution of the field arising from a one-dimensional (Ising-like) field distribution. The important result to note for this case is that $P(H=0)=0$, whereas $P(H_I=0)\neq 0$.

Kondo's[10] recent calculation of the thermoelectric power shows that $P(H=0)$ is finite (nonzero), indicating that an Ising-like[11] probability distribution of H is observed experimentally.

The purpose of this note is to show that (a) using the $P(H)$ result from the thermoelectric power, ΔC_v near $T=0$ from model I is proportional to $-T\log T$, which is not observed experimentally,[12] and (b) a reasonable upper limit to the excess specific heat from model I, even if one does not use a probability distribution of fields, is only about one-third of the experimentally observed value.

Calculations. – The enhancement factor of the density of states is $1+\alpha$, where α is given by Eq. (28) of Kondo's paper[2]:

$$\alpha = \frac{3zSJ^2c}{2\epsilon_F}\left\langle\frac{1}{2\mu_B H}\right\rangle, \tag{1}$$

where z, S, J, c, and ϵ_F are the number of conduction electrons per atom, the impurity spin, the strength of the s-d interaction, the impurity concentration, and the Fermi energy, respectively. The bracket $\langle\,\rangle$ indicates an average over all impurity sites, and

$$2\mu_B H = \left(\frac{3z}{2}\right)^2\left(\frac{4\pi J^2}{\epsilon_F}\right)\sum_{n\neq m} F(2k_F R_{nm})\langle S_m\rangle, \tag{2}$$

where R_{nm} is the distance between the impurity sites n and m, k_F is the Fermi wave vector, and $F(x) = (x\cos x - \sin x)x^{-4}$.

Now we use the result that $P(H=0)\neq 0$ from the thermoelectric power[10] to calculate α. We have

$$\alpha = \frac{3zSJ^2c}{2\epsilon_F}\int_{\Gamma\mathit{\Gamma}}^{\infty} P(H)H^{-1}dH, \tag{3}$$