cal model.[7] The results are much the same but for conciseness we quote for the latter at the melting point when the data are the same for each alkali. We find $a_{00}=0.39$, $a_{01}=-0.20$, $a_{02}=0.08$, $a_{11}=0.18$, $a_{12}=-0.10$, and $a_{22}=0.10$. (The elements involving P_3 have also been calculated and are included in our calculations, but they are unimportant.)

If we now take the η's in Table I of Young, Meyer, and Kilby,[8] it is a trivial matter to compute corresponding η^{mt}'s. These may be compared with those obtained by Lee[2] by fitting experimental Fermi-surface data (see his Table IV). Lee gives various alternatives depending upon the Fermi energy assumed. No matter how one selects, one obtains the feature noted by Lee of the strong *p* phase shift for Li, the intermediate case of Na, and the increasingly important *d* phase shifts for K, Rb, and Cs. To be specific, we plot the free-electron values in Fig. 1 and agreement will be seen to be satisfactory.

Muffin tins and pseudopotentials, while in principle equivalent, each appear to have their own practical advantages. The former possess the smaller phase shifts and might therefore yield the more accurate answers in any formula based on perturbation theory. Calculations of densities of states in solids[3] might be one example of this. On the other hand the use of pseudopotentials takes into account the fluctuations which the mean muffin-tin potential misses (Fig. 1 of Ref. 4). This consideration might be of overriding importance in the Ziman formula for the resistivity of a liquid metal.[4] Indeed our calculations,[8] particularly of the thermopowers (which are much more sensitive to the approximation used), suggest this.

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MAGNETIC CIRCULAR POLARIZATION OF THE Tl LUMINESCENCE IN KI:Tl[†]

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The magnetic-field–induced circular polarization of the Tl characteristic emission in KI:Tl has been studied. The large size of the effect and its temperature dependence indicate that the emitting state sampled by our measurement is nearly degenerate. The data obtained support the theory on Tl^+ luminescence in alkali halides recently proposed by Fukuda.

The optical properties of Tl^+ in the alkali halides are greatly influenced by the large spin-orbit interaction that characterizes heavy-metal ions. Recent experimental and theoretical work has shown that the excited states of the Tl^+ center are also characterized by strong dynamic and static Jahn-Teller interactions.[1] The simultaneous existence of large spin-orbit and Jahn-Teller effects may have a marked influence on the electronic states of the Tl^+ ion, as shown recently by Fukuda[2] in his theory of the luminescent states of Tl^+ in the alkali halides.

We have investigated the effects of a magnetic field on the relaxed excited states of Tl^+ in KI:Tl through the analysis of the field-induced circular polarization of the 2.88-eV emission. The results, although not conclusive, are in good agreement with qualitative predictions from Fukuda's theory.

Samples of KI:Tl (Tl concentrations $\sim 10^{-2}$ and 5×10^{-4} mole%) were placed in the bore of a small superconducting solenoid immersed in liquid helium. The sample temperature could be varied from 4.2 to 1.3°K and the magnetic field up to 25 kG. The 2.88-eV emission was excited in the *D* band at 5.51 eV with a H_2 lamp through a monochromator, an interference filter, and quartz optics. The emitted light was viewed through Pyrex optics along the magnetic-field axis and was analyzed for its left- and right-circular polarization by an electro-optic light modulator. The light was then collected through a

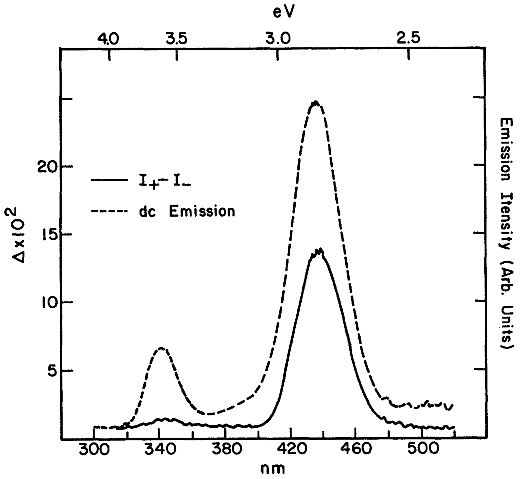

FIG. 1. ac (solid line) and dc (dashed line) signals obtained at 1.3°K with $H_{-z}=23$ kG. Excitation was in the D band at 5.51 eV. Tl^+ concentration ~10^{-2} mole%.

monochromator (band-pass ~15 nm) by an EMI 9558Q photomultiplier. Both dc and ac components of the signal were recorded simultaneously, the latter after synchronous detection.

In Fig. 1 we show a typical signal obtained with a field of 23 kG at a temperature of 1.3°K. This signal corresponds to a zero-moment change Δ of 13% where Δ is defined as $(I_+-I_-)/I$, and I is the total intensity emitted in the 2.88-eV band at zero field. The zero-moment change favors emission of left-circularly polarized light $(x+iy)$ when the magnetic-field vector is opposite to the propagation vector of the light. The values of Δ and its behavior with field seem to be independent of Tl concentration, at least up to 10^{-2} mole%. No reproducible data for the first-moment change could be obtained, and this places an upper limit of about 1% of the bandwidth on its value, since the noise in our signal was about 10%.

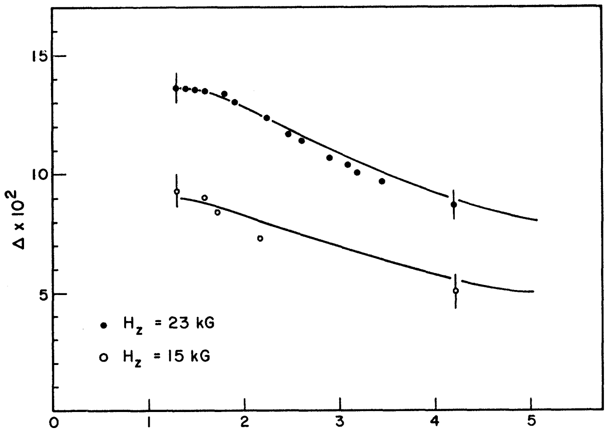

FIG. 2. Temperature dependence of the circular polarization of the 2.88-eV emission induced by magnetic fields of 15 and 23 kG. Excitation in the D band. Tl^+ concentration ~10^{-2} mole%. The solid lines represent Eq. (1) with $\delta=5.7\times10^{-4}$ eV.

The signal was found to decrease by 35% as the temperature was increased to 4.2°K. In Fig. 2 we show the results of two temperature runs, taken at the fields of 23 and 15 kG, respectively. At both fields a saturation of the signal with decreasing temperature seems to take place. The field dependence of the signal is shown in Fig. 3 at the temperatures of 4.2 and 1.3°K, respectively. The deviation from linearity is reproducible and not within the experimental error, at least for the samples with higher Tl concentration. We have at the present time no simple explanation for this deviation. Therefore in what follows we shall approximate the experimental behavior with a straight line.

The 3.70-eV emission also showed a field-induced zero-moment change (see Fig. 1). The signal had the same sign as that of the 2.88-eV emission, but since its size was much smaller it was not investigated further.

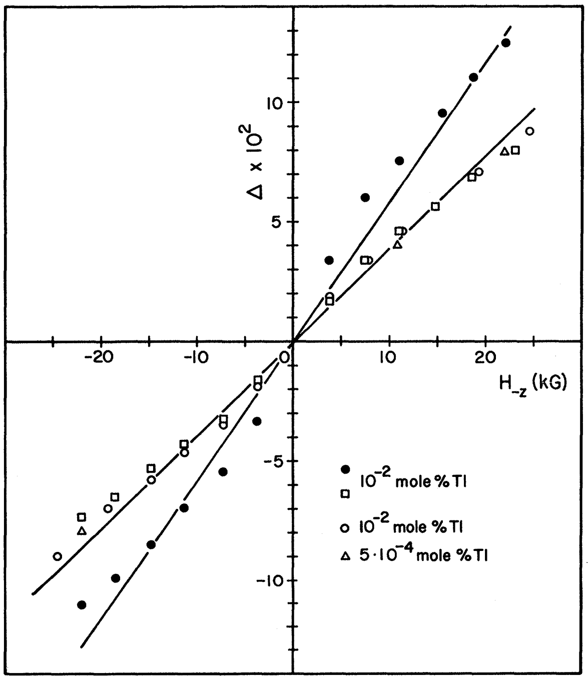

FIG. 3. Field dependence of the circular polarization of the 2.88-eV emission excited in the D band at 1.3°K (closed symbols) and 4.2°K (open symbols). The data taken at 4.2°K indicate there is no sample or concentration dependence of the signal. The solid lines represent Eq. (1) with $\delta=5.7\times10^{-4}$ eV.

In what follows we shall attempt to interpret phenomenologically the temperature dependence of Δ and a linear approximation to its field dependence. The low-temperature saturation of Δ indicates that the magnetic field has predominantly a mixing effect. A dominant splitting contribution would in fact behave as $1/T$ for the size of Δ found in our experiment. The large size of the signal, however, indicates that the states that are mixed by the field are nearly degenerate. Shepherd[3] observed a behavior of a magnetic-field-induced zero-moment change versus temperature similar to the one depicted in Fig. 2; in his case the system was the doublet E ground state of the R center in KCl. He found that he could accentuate the saturating behavior of Δ by applying an external stress simultaneously with the magnetic field. He therefore attributed the saturating behavior when no external stress was applied to a removal of the E degeneracy by internal random strains. Such a phenomenon should be quite general, as long as one has a degenerate state.

Our results can then be explained by assuming that the emitting state sampled by our measurement consists of two, or possibly more, nearly degenerate levels.

Recently Fukuda[2] has proposed a theory based on the Jahn-Teller effect which systematically predicts the major features of Tl$^+$ emission in most alkali halides. Considering the ${}^3T_{1u}({}^3P_1)$ and ${}^3A_{1u}({}^3P_0)$ adiabatic potential surfaces in the six-dimensional a_{1u}, e_g, t_{2g} space,[4] he shows that both sheets have two kinds of minima in the e_g subspace. For KI:Tl, the minimum assigned to the 2.88-eV emission consists of an upper level of E_u symmetry and a lower level of A_{1u} symmetry. These levels are not in thermal equilibrium with each other, as shown by lifetime studies of their separate contributions to the 2.88-eV emission.[5] Excitation in the D band at 4.2°K yields both components[6] of the 2.88-eV emission with approximately equal efficiency.[5]

Let us now examine the effect of an applied magnetic field H_z on this system. Since our measurements imply no sizable splitting effect of H_z we assume that the E_u level is not degenerate, but nearly so, the splitting energy being δ. The energy separation between the A_{1u} and E_u levels is expected to be much larger than δ and therefore we shall neglect the mixing of A_{1u} and E_u levels by the magnetic field. On the other hand, the emission from the ${}^3A_{1u}$ state will influence the denominator of $\Delta = (I_+ - I_-)/I$, and therefore in order to compare theoretical predictions of Δ with the data, we shall multiply the former by $\frac{1}{2}$.[5]

The dominant contribution to Δ will come from the mixing by the magnetic field of the strain-split E_u levels. A simple adaptation of Shepherd's calculation[3] to our case yields

$$\Delta = -\frac{\bar{g}\beta H}{\delta} \tanh \frac{\delta}{2kT}, \tag{1}$$

where $\bar{g}$ is the effective g factor of the E_u level. Within Fukuda's model, $\bar{g} = g_A$, where g_A is the g factor of the A band in absorption. Onaka <u>et al.</u>[7] have reported the value of 0.61 for the effective g value of the A band at 77°K. Assuming $\bar{g} = 0.6$, Eq. (1) will fit the data well if

$$\delta = 5.7 \times 10^{-4} \text{ eV}.$$

The resulting curves are depicted by the solid lines in Figs. 2 and 3, respectively. The value of δ obtained is satisfyingly close to the random-strain splittings obtained in other systems.[3,8] The fact that Eq. (1) fits the data, using this very reasonable value for the one unknown parameter, is good evidence in support of Fukuda's model.

We must caution, however, that our data <u>alone</u> cannot unambiguously exclude other models for the 2.88-eV emission. The main experimental conclusion from our data is that the emitting state is split but still nearly degenerate. The perturbed-exciton model[1,9] for the 2.88-eV fast emission may also lead to agreement with the data, although in a less simple fashion. In this respect a measurement of the effective g value of the self-trapped triplet exciton state[10] of pure KI should provide the additional information that is needed to test whether the perturbed-exciton model is quantitatively consistent with these data for the Tl$^+$ luminescence.

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PHOTOCONDUCTIVITY IN DISORDERED NICKEL-OXIDE FILMS*

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Photoconductivity measurements in the infrared and visible spectral regions have been made on disordered NiO films. The result shows a prominent peak at the energy of 0.23 eV, coinciding with the one in the infrared absorption, which is believed to be a spin-excited state due to the antiferromagnetic ordering. We propose a model to explain the observation.

We report here an experimental result of transport properties in very thin nickel-oxide films. These films, of approximately 50 Å thickness, were prepared at room temperature by vacuum evaporation of pure nickel at 10^{-6} Torr on polished sapphire substrates and subsequent oxidation in air. Then the specimens were heat treated at 10^{-2} Torr of residual air at 300°C for half an hour. Electron diffraction studies of films prepared by the same procedure show that crystallite sizes are less than 20 Å, indicating that the films are essentially in a disordered state.

Two vacuum-deposited nickel electrodes, separated by 75 μm, were used for photoconductivity as well as for electrical conductivity measurements. Although pure NiO crystals are usually good insulators, we have found that this disordered film is a semiconductor. Figure 1 shows the resistance R as well as the activation energy E_a, defined by $R = R_0 \exp(E_a/k_BT)$, as a function of reciprocal temperature. The activation energy E_a, which is about 0.5 eV at 500°K, decreases monotonically down to 0.003 eV at 20°K. This is reminiscent of the electrical conduction in $Li_xNi_{1-x}O$ crystals.[1]

We have measured the spectral response of the photoconductivity for photon energies between 0.15 and 4 eV over the temperature range from room temperature to 5°K. This is probably the first observation of infrared photoconductivity in NiO.[2] We have found a prominent peak at 0.23 eV on a background that increases with the photon energy. The result at 20°K is shown in Fig. 2. The half-width of the peak seems to be independent of temperature, although it is barely observable at room temperature presumably because of decreasing carrier lifetime with increasing temperature. It is unlikely that any impurity level gives rise to such a sharp peak, particularly in a disordered system. We have also eliminated heat effects as a possible cause of this observation. We might add here that an unsuccessful attempt has been made to see this photoconductivity peak in monocrystalline NiO.

It is informative to compare our result with the absorption curve of monocrystalline NiO obtained

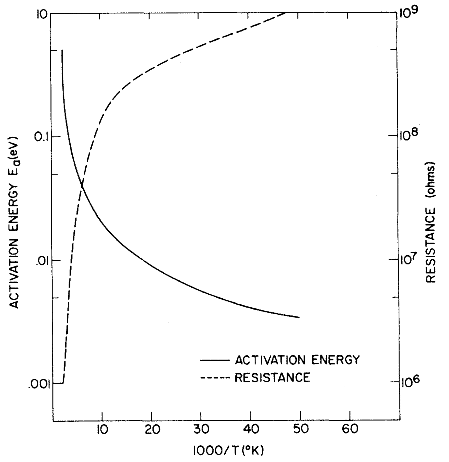

FIG. 1. Semilog plot of resistance R and activation energy E_a, defined by $R = R_0 \exp(E_a/k_BT)$, vs $1/T$.