†National Science Foundation Cooperative Fellow, 1963-1964.

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M_A CENTERS IN ADDITIVELY COLORED KCl

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Strong evidence now exists that an F_A center is simply an F center with an impurity ion at a nearest-neighbor site.[1-4] While similarly perturbed centers involving F aggregates would likewise be expected, their existence has not been clearly demonstrated. The purpose of the present note is to report evidence in KCl of the simplest such association, an M center with a Na$^+$ ion neighbor, i.e., an M_A center.

The usual M center consists of two nearest-neighbor F centers along a ⟨110⟩ lattice direction.[5-6] Its main transition, the M band, lies on the low-energy side of the F band. Figure 1 shows the absorption in this spectral region for three crystals which differ primarily in their Na$^+$ concentration. Curve *a* shows the M band in an undoped crystal with a natural content of 0.003 mole% NaCl. Compared to this spectrum, curve *b* reveals a weak absorption at about 820 mμ in a crystal with 0.04 mole% NaCl. The relative size of this shoulder absorption increases for crystals with increasing NaCl content until it predominates. This is evidently the case for a crystal containing 0.35 mole% NaCl, as shown in curve *c*. Similarly, the size of the F_A band (at about 580 mμ) relative to that of the F band is very small for the crystal of Fig. 1, curve *a*, but is comparatively larger for crystals with increasing Na$^+$ concentration.

The M center has three symmetry axes along which its optical dipole moments lie. One is the ⟨110⟩ vacancy axis, which is the direction for the M band. The other two are the ⟨110⟩ and ⟨100⟩ directions perpendicular to this axis. M-center transitions with moments along these normally overlap the F band. A common pro-

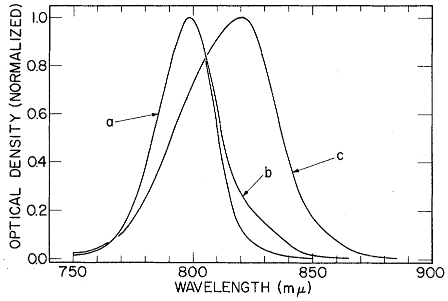

FIG. 1. Absorption spectra measured at liquid-helium temperature for three crystals differing in Na$^+$ content. Curve a refers to an undoped sample (actually containing 0.003 mole% NaCl); curve b refers to a sample with 0.04 mole% NaCl; curve c refers to a crystal with 0.35 mole% NaCl.

cedure for determining these is to measure the F absorption with polarized light after reorienting M centers with polarized F light at low temperatures.$^{7-10}$ It turns out that both the $\langle 110\rangle$ and $\langle 100\rangle$ transitions in the F region are effective in causing reorientations.

Specifically, to determine the $\langle 110\rangle$ M-center absorptions one might expose a crystal containing F and M centers to F light propagating in the [100] direction with electric vector oriented in the [0$\bar{1}$1] direction. The dichroic spectrum, which is the absorption difference, [011] $-$[0$\bar{1}$1], for light again propagating in the [100] direction, contains only the $\langle 110\rangle$ M-center transitions. The reason for this is that the subtraction effectively removes absorptions due to isotropic centers like the F center, and also the $\langle 100\rangle$ M-center bands, since dichroism is not induced in these using this experimental arrangement.

The $\langle 100\rangle$ M transitions can be determined from $\langle 100\rangle$ dichroic spectrum using the same arrangement after orienting with light polarized in the [010] direction. This situation, however, is complicated by the fact that [010] light induces dichroism in both sets of transitions. However, the actual $\langle 100\rangle$ transitions are easily determined as follows: It can be shown that when the $\langle 100\rangle$ and $\langle 110\rangle$ dichroic spectra are scaled for equal M-band dichroism, then the contributions of the $\langle 110\rangle$ transition in the vicinity of the F band have the same magnitude but opposite sign. Thus, addition of the $\langle 100\rangle$ and $\langle 110\rangle$ dichroic spectra gives the $\langle 100\rangle$ transition.

Figure 2 shows dichroic spectra for two crystals in which the centers giving the absorption in the M-spectral region were oriented first with [0$\bar{1}$1] F light and then with [010] F light. The solid curves relate to a crystal with dichroism due almost entirely to the centers giving the 820-mμ absorption. This was accomplished by preparing a crystal with spectrum similar to Fig. 1, curve c, and exposing it to polarized F light at liquid-helium temperature for a relatively short period of time. A separation is possible since these centers reorient much more rapidly than M centers. One also avoids F_A-center reorientations at this low temperature.^{3} The dashed curves shown in Fig. 2 refer to a crystal with oriented M centers alone.

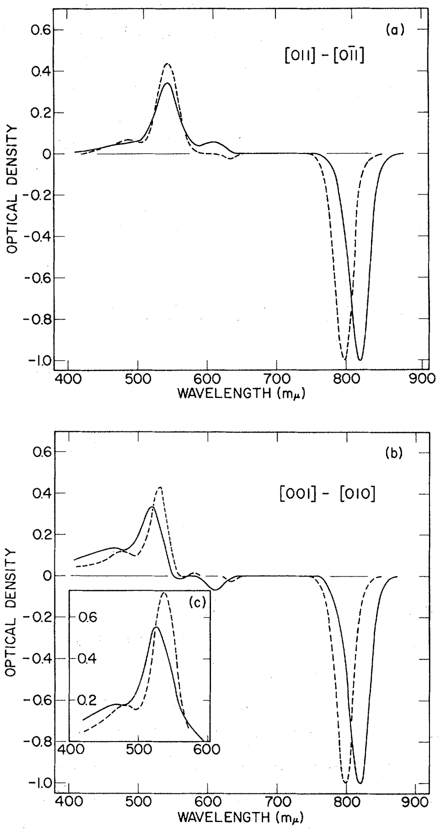

FIG. 2. Normalized dichroic spectra measured at liquid-helium temperature for two crystals; one containing only oriented M_A centers (the solid curves), the other containing oriented M centers alone (the dashed curves). M_A centers were oriented at liquid-helium temperature; M centers, at about 200°K. (a) The difference in absorption, [011]$-$[0$\bar{1}$1], after orienting with [0$\bar{1}$1] F light. These give the $\langle 110\rangle$ transitions. (b) The difference in absorption, [001]$-$[010], after orienting with [010] F light. (c) The sums ([001] $-$[010])+([011]$-$[0$\bar{1}$1]). These give the $\langle 100\rangle$ transitions.

It is evident from these curves that the two centers are similar in several important respects. Their absorptions in the M region exhibit both ⟨110⟩ and ⟨100⟩ dichroism, consistent for a ⟨110⟩-type center. Each has similar transitions in the F region with correspondingly oriented dipole moments. By contrast, the M-center's ⟨100⟩ absorption bands in the F region lie at slightly longer wavelengths than those of the new center. Moreover, the new center has an absorption at 610 $\mathrm{m}\mu$, on the long-wavelength side of the F band, not present in the M-center spectrum while the M center has a weak absorption at 634 $\mathrm{m}\mu$ absent in the new center.

The over-all similarity in both the behavior and the absorption of the two centers leads one to conclude that the new center is simply a perturbed M center. From its dependence on impurity concentration it is very likely perturbed by a neighboring Na^+ ion.[11]

Unlike the F center, the M center has several nonequivalent nearest-neighbor sites. If these were equally likely, one would possibly observe several overlapping bands in the M region. The fact that one transition is observed predominantly is an indication that one configuration is most probable. From the over-all differences in the M and M_A spectra, it is likely that the Na^+ ion lies somewhere in the (100) plane containing the M center. The substitutional site along the ⟨110⟩ direction bisecting the center would give a configuration with the highest coordination and symmetry, and is considered the most reasonable alternative.

Na^+ has always been a rather common impurity found in KCl crystals, particularly a number of years ago. Thus, M_A centers could have formed in earlier studies along with the usual M centers during the F-aggregation process. This is suggested by the variation in reported M-center properties such as the M-band peak value.[12] It is hoped that the results of the present investigation will provide a new basis for possibly understanding these former anomalous effects.

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