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Inversion Symmetry of *M* and *R* Centers*

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The energy states of color centers lacking inversion symmetry will generally possess permanent dipole moments. Consequently the optical absorption bands of such centers will exhibit linear stark effects and should become dichroic in large electric fields. No dichroism for the *M* or *R* bands in NaCl or KCl was observed at 78°K as a result of applied fields of 3×10^5 v/cm. Since the sensitivity of the measurement was several hundred times greater than that required to detect the field-induced dichroism calculated for a model lacking inversion symmetry, it is tentatively concluded that *M* and *R* centers possess inversion symmetry.

A. INTRODUCTION

The atomic models of R_1, R_2, and M centers (in alkali halides) proposed tentatively by Seitz[1] are shown in Fig. 1. The R_1 and R_2 centers are presumed to consist of one and two electrons, respectively, trapped at a complex of two adjacent negative-ion vacancies. The center assigned to the M-absorption band is one electron trapped at a complex of two adjacent negative-ion vacancies and a positive-ion vacancy. All three models have at most twofold rotation axes, and this limited symmetry should possibly manifest itself in experiments employing polarized light.

The experiment of Ueta,[2] in which the M-band absorption in KCl was made dichroic by bleaching with M-band light polarized parallel to a (1,1,0) crystal direction, proves that the M center lacks complete cubic symmetry. His results are consistent with either of the three models shown in Fig. 1, and are also consistent with models having a (1,1,1) axis as the important symmetry axis. Only models with a (1,0,0) axis are excluded by Ueta's experiment. The experiments of Feofilov[3] on LiF and NaF and of Lambe and Compton[4] on NaCl and KCl, which determined the polarization of the luminescence excited by irradiation with polarized light in the M band, prove that the important axis of the M center has a (1,1,0) direction (as is the case for the models shown in Fig. 1). Similar experiments by Lambe and Compton[4] on the R bands in NaCl and KCl are less conclusive and allow perhaps a (1,1,1) axis as well as a (1,1,0) axis.

It is impossible to distinguish between the R-center and M-center models of Fig. 1 by optical experiments of the type described above. The important difference in symmetry between the models is that the R-center models possess inversion symmetry, whereas the M-center model does not. Paramagnetic resonance experiments might distinguish the symmetries provided the structure associated with hyperfine interactions is resolved. Lord[5] and Kawamura and Ishiwatari[6] have reported observation of the M-center resonance in LiF and KCl, respectively, but in both cases the resonance is broad and is superposed on a larger F-center resonance.

A basis for detecting the absence of inversion symmetry is provided by the Stark effect. A well-known quantum mechanical theorem states that nondegenerate stationary states of a system possessing inversion symmetry have zero dipole moment. Consequently such systems will show only second order Stark effects. On the other hand, quantum states of systems lacking inversion symmetry will generally possess dipole moments and will suffer first order shifts by an applied electric field. Therefore, if the M-absorption band is associated with the M-center model of Fig. 1, linear Stark shifts of the band are likely observable.

B. THEORY OF THE EXPERIMENT

The symmetry axis of the M-center model is the twofold rotation axis lying in the plane of the three vacancies and bisecting the line joining the two negative-ion vacancies. The symmetry of the center is so restricted that all quantum states are nondegenerate. The energy levels of such a center have been investigated by Inui, Uemura, and Toyozawa[7] using the

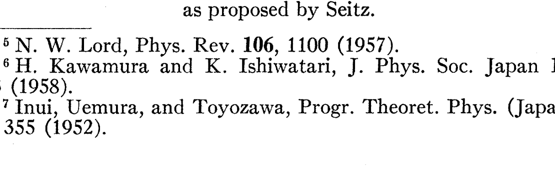

FIG. 1. Atomic models of R_1, R_2, and M centers, as proposed by Seitz.

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method of linear combination of atomic orbitals and by Gourary and Luke[8] using the point-ion lattice method. The optical transition between the ground and first excited state is allowed if the polarization vector of the light is along the line joining the two negative-ion vacancies (perpendicular to the axis). The electric dipole moments of all states are directed along the axis.

In a dc electric field $\mathbf{E}$ the energy levels of the ground and first excited states will be shifted, so that the change, w, in transition energy is given by

$$w=\Delta\mathbf{p}\cdot\mathbf{E}_{\text{local}},$$

where $\Delta\mathbf{p}$ is the difference in dipole moment of the ground and excited state. The correct local field is of course unknown, so we shall use the Lorentz local field as an approximation:

$$E_{\text{local}}=(\epsilon+2)E/3,$$

where ϵ is the static dielectric constant. In view of the Franck-Condon principle Δp should not include ion position readjustments, and may therefore be estimated from the electronic wave functions alone. We have computed Δp from the wave functions given by Gourary and Luke[8] for NaCl, and find

$$\Delta p\sim 5\times 10^{-18}\text{ cgs units.}$$

This value is probably too large, especially since the variational wave function derived for the excited state did not allow polar asymmetry. One should also emphasize that it is generally difficult to obtain wave functions sufficiently accurate to predict reliable dipole moments. The above value is at most indicative of a possible order of magnitude. For an applied field of 3×10^5 v/cm the estimated shift in absorption energy is

$$w\sim 8\times 10^{-3}\text{ ev.}$$

Were all the M centers oriented in the same direction, such an energy shift could be detected by standard optical absorption techniques. Unfortunately the twelve possible M-center model orientations will be equally represented, and the first order effect of the electric field will cancel. As shown below the absorption line will not be shifted at all, but will suffer only a small change in shape.

Consider a cube of material oriented so that an electric field can be applied along a (1,0,0) direction and light is transmitted along a (0,1,0) direction. We shall compute the absorption coefficients, $\mu_{\parallel}(W)$ and $\mu_{\perp}(W)$, associated with polarization of the light parallel and perpendicular to the electric field, respectively, where W is the quantum energy of the light. The twelve orientations of the M-center models fall into three categories, A, B, and C, whose symmetry axes lie in the (1,0,0), (0,1,0), and (0,0,1) planes, respectively. The A-type centers will be unshifted by the field because their dipoles are perpendicular to the field. The B- and C-type centers will suffer shifts in transition energy of $\pm w/\sqrt{2}$ because their dipoles are inclined 45° with the field. Light polarized parallel to the field is absorbed by B- and C-type centers, so that the absorption coefficient is

$$\mu_{\parallel}(W)=\tfrac{1}{2}\mu(W+w/\sqrt{2})+\tfrac{1}{2}\mu(W-w/\sqrt{2}),$$

where $\mu(W)$ is the absorption coefficient in the absence of a field. Light polarized perpendicular to the field is absorbed by A- and B-type centers, so that the absorption coefficient is

$$\mu_{\perp}(W)=\tfrac{1}{2}\mu(W)+\tfrac{1}{4}\mu(W+w/\sqrt{2})+\tfrac{1}{4}\mu(W-w/\sqrt{2}).$$

Realizing the smallness of w relative to the width of the absorption line, one may expand the above expressions in power series in w. If higher terms are dropped, they become

$$\mu_{\parallel}(W)=\mu(W)+w^2\mu''(W)/4,$$
$$\mu_{\perp}(W)=\mu(W)+w^2\mu''(W)/8.$$

Because the second derivative of a symmetric absorption curve is also symmetric about the center of the band, the effect of the electric field is merely to broaden the band, and by an amount proportional only to the square of the field. The largest change in absorption coefficient is at the center of the band ($W=W_0$). For a Lorentzian band shape,

$$\mu''(W_0)=-2\mu(W_0)/\Gamma^2,$$

where Γ is the half-width of the band. If we define

$$\Delta\mu\equiv\mu_{\perp}(W_0)-\mu_{\parallel}(W_0)=\mu(W_0)-\mu_{\perp}(W_0),$$

the relative change in absorption coefficient resulting from the field is

$$\Delta\mu/\mu=\tfrac{1}{4}(w/\Gamma)^2.$$

Since the half-width of the M band in NaCl at 78°K is about 0.05 ev, the relative change expected is

$$\Delta\mu/\mu\sim 6\times 10^{-3}.$$

Such a small change can be detected relatively easily by modern ac methods using phase-sensitive detectors. One may apply an alternating electric field to the crystal and detect the ac component of the transmitted light, or one may rotate the plane of polarization of the light and detect the ac component of transmitted light introduced by the application of a dc electric field. The latter method was chosen and is described below.

C. EXPERIMENTAL METHOD

The experimental apparatus employed to detect a linear Stark effect in M- or R-band absorption consisted of the following (in functional order): monochrometer, lens, rotating polaroid film (20 rev/sec), compensator, lens, cryostat, crystal, 30 kv dc power supply, lens, infrared photomultiplier, 40-cycle tuned amplifier, and phase-sensitive detector.

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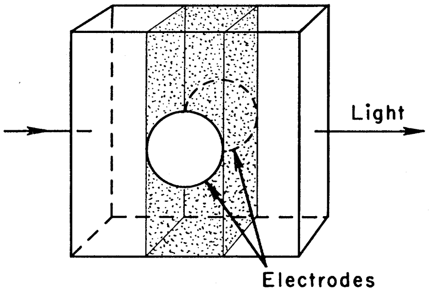

FIG. 2. Schematic illustration of sample geometry.

The compensator consisted of a piece of polaroid film and was used to eliminate the ac component of the light incident on the crystal by critically adjusting the angle of the polaroid and the fraction of the beam intercepted. This operation was made necessary because light from a monochrometer is appreciably polarized. Consequently the rotating polaroid introduces a large ac component. In compensating the system (a procedure necessary at each wavelength) it is necessary to employ also an ac (nonphase-sensitive) detector in order to minimize the amplitude of the signal as well as the phase-sensitive component.

The samples, cleaved from Harshaw single crystals of NaCl and KCl, were approximately 2 cm square and 1 mm thick. As illustrated in Fig. 2, only a portion of each specimen (6 mm×2 cm) was colored (by x-rays) so that light absorption occurred only in regions between the electrodes. The optics were adjusted so that an image of the exit slit of the monochrometer was located between the electrodes, and only light traversing the crystal without reflection from the 2×2 cm faces was allowed to reach the photomultiplier. The samples were colored with 90-kv x-rays, filtered by $\frac{1}{8}$ in. of Al, and subsequently irradiated in the tail of the F band to enhance the M and R bands. Optimum sensitivity required that the peak absorption coefficient of the bands (at 78°K) be about 2 cm^{-1} (corresponding to concentrations of centers of about $10^{16}/\text{cm}^3$), and these conditions were achieved. All measurements were at 78°K.

The ac signal arising from the application of 30 kv across the 1 mm dimension of the crystal was the observation of interest, since the rotating polarized light is alternately absorbed by centers roughly parallel and perpendicular to the electric field. Calibration of the apparatus was made by inserting a Polaroid film into the light beam (at reduced amplifier gain).

D. RESULTS

No dichroism arising from an applied field of 3×10^5 v/cm was observed for the M bands in NaCl and KCl or for the R_1 and R_2 bands in KCl. The sensitivity of the apparatus allowed the following upper limit on the dichroism in these cases:

$$\Delta\mu/\mu<3\times10^{-5}.$$

This limit is 200 times smaller than the estimate obtained in Sec. B, based on the M-center model. One may conclude that an upper limit on the dipole moment difference in each case is 0.4×10^{-18} cgs unit.

The foregoing conclusion applies only if the dipole moments are oriented in (1,0,0) or (1,1,0) directions. No dichroism is expected for dipoles having (1,1,1) directions when subjected to an electric field in a (1,0,0) direction. The field should be applied in a (1,1,0) direction to observe dichroism in this case. For this reason samples of KCl were prepared with the 2×2 cm faces having (1,1,0) orientations. Again no field-induced dichroism was observed in the M, R_1, or R_2 bands. This orientation is also more favorable for observing the dichroism of centers having (1,1,0) axes, since a calculation analogous to that in Sec. B predicts a larger dichroism, by a factor of two, for the same dipole moment difference. We conclude that the upper limit on the dipole moment difference for M or R centers, irrespective of the orientation of their principle axis of symmetry, is

$$\Delta p<0.3\times10^{-18} \text{ cgs unit.}$$

E. CONCLUSION

Since the upper limit for the difference in dipole moment between ground and excited states, established above, is an order of magnitude smaller than that expected for a center lacking inversion symmetry, it seems appropriate to conclude from these results that M and R centers possess inversion symmetry. The weak point in the argument is the uncertain reliability of using the one-electron wave functions of Gourary and Luke[5] for estimating dipole moments. Nevertheless, the M- and R-center models should probably be revised. In this regard the arguments of Herman, Wallis, and Wallis,[9] which suggest that the R_1 and R_2 bands may arise from two excited states of the same center, reduce the diversity of models required.

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