the formation of a fairly broad, Lorentzian line for heavily damaged crystals.

If *F*-centers come together in pairs, and if their electron spins form a triplet state, the resonance line will remain Gaussian, but the second moment will be smaller by a factor of 2. For progressively larger groupings, the line shape should gradually change to a Lorentzian.

Lazarus, D.: I wonder if you have any values for the lattice contraction about the *F*-center, or justification for this? From high-pressure studies of diffusion and ionic conductivity, it can be concluded that the volume of neutral vacancies is somewhat larger than the ionic volume, for both positive and negative ion vacancies.

Slichter, C. P.: One must distinguish between *F*-centers and neutral vacancies. The latter expand since the missing charge helped to hold the lattice together. With an *F*-center, two competing effects arise. The electron tries to pull the lattice in, but since it is somewhat more diffuse than the ion it replaces, it is not as effective for the close atoms. On the other hand, the missing ion possessed inner shell electrons which help to prevent a lattice contraction. The absence of these repulsive forces favors an inward collapse.

Detailed calculations have been made for the *F*-center in LiF, but different theorists have come to opposite conclusions as to which effect prevails.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT II, 1963

Electron Spin Resonance of Electron-Excess Color Centers in KCl Crystals

Hiroshi OHKURA AND Kazuo MURASE

Department of Applied Physics, Osaka City University, Osaka, Japan

Electron spin resonances for various kinds of electron-excess color centers have been carried out. Non-magnetism of the F' and M center is confirmed. The study of sodium-A centers verifies the model proposed by Nishimaki, Kojima and Lüty. The result on the B center shows the consistency with Mieher's *ENDOR* result.

The paramagnetism associated with the Z_3 center was found, but that of the Z_2 center could not be detected. These results are inconsistent with the proposed models by Pick and Seitz. To explain our results, two alternative models are proposed for the Z_2 center, *i.e.* a pair of divalent ions trapping two electrons, or the association of an F center and a divalent ion that has trapped an electron. The Z_3 center is proposed to be an ionized Z_2 center.

1. Introduction

The electron spin resonance study of the color centers in alkali halide crystals is very important not only for the verification of their proposed models, but also for the determination of their electronic structures. A few studies have been carried out for the electron-excess color centers other than the F center.[1)]

When the colored *KCl* crystals doped with *NaCl* are irradiated with the F light at $-30°C$, two absorption bands appear at the expense of the F band. These have been named A_1 and A_2 band, and found to arise from a common species of centers called A centers by Nishimaki, K. Kojima and T. Kojima,[2)] and Lüty,[3)] independently. They proposed a model (NKL's model) for the A center as an F center in which one of the six nearest neighboring potassium ions has been substituted by a sodium ion. Similar results are obtained for *Li*-doped *KCl* crystals.

Two absorption bands are also obtained by

F light irradiation at room temperature, but one of them has a slightly different peak energy from that of A_1 band. These two bands were first reported by Ishiguro and Sugioka,[4] and was denoted tentatively as the B center by Lüty.[3] Recently, Mieher resolved hyperfine structure of the *Li-B* center by using the *ENDOR* technique[5] and found the displacement of the *Li* ion toward the *Cl* ion site in NKL's model.

Since the discovery by Pick,[6] four kinds of Z centers have been found in the colored *KCl* crystals doped with divalent ion. Additively colored *KCl:Sr* quenched to room temperature from 400°C or above displays only F band absorption as does undoped *KCl*. However, the new absorption bands appear at the expense of the F band by the irradiation of F light and other treatments. Up to now, only a partial picture has emerged about these bands. The *ESR* study has not been performed except for Z_1 centers.[7]

Recently, Miyamoto, Nakashima and Mizuno[8] reported that the K band corresponds to the optical absorption of the F center that has been trapped by dislocation lines in *KCl* crystals. Their idea, however, seems not to be plausible in view of the energetic consideration and correlation of the optical densities of the K band and dislocation lines.

In this paper, we shall report the results of *ESR* (1) on F', K and M centers in undoped crystals, (2) on A and B centers in *Li-* or *Na*-doped crystals, and (3) on Z_2 and Z_3 centers in *Sr*-doped crystals.

The *ESR* measurements were carried out by using the X band microwave with high frequency modulation of 455 kc/sec. The maximum sensitivity of the *ESR* apparatus corresponds to 2×10^{12} spins per gauss. Passage effects which are caused by high frequency modulation were taken into account in analyzing data in every case.[9] Special attention was paid in preparing the resonant cavity. The specimen was laid just over the elliptic-shaped hole, which was bored at the central portion of the bottom of the cavity, to permit the entry of the F band light through a copper pipe, which was connected to the hole to prevent leakage of microwave power from the cavity. The cavity had a series of slots parallel to the narrow face of the wave-guide to admit the magnetic field modulation of 455 kc/sec.

The crystals were additively colored at 550°C in potassium vapor; the density of color centers was $1\sim2\times10^{17}/cm^3$ for all samples used in our experiments.

2. Experimental Results

Undoped KCl crystals

During the optical conversion process in $F\rightleftarrows F'$, the *ESR* signal does not change in its significant properties, namely, line shape (Gaussian, whose half width is 58 ± 1 gauss), g-value (1.995) and passage condition, but its intensity changes proportionally to the optical density of the F band. One of the typical recorder traces is shown in Fig. 1, which was recorded by adjusting the apparatus at the peak of the derivative of χ' at −100°C, against irradiation time of various kinds of wave-length marked by arrows in the figure. The straight line drawn under the recording trace shows the base line. Irradiation processes were carried out from right to left subsequently. By the irradiation of F band light, the intensity immediately dropped to about one-third of its initial height. It was recovered completely by F' light irradiation. Thermal recovery of the F center is also tested, though not shown in the figure. Immediately after turning off the F band light at −50°C, *ESR* signal of the F center was recovered in the dark with a relaxation time of 22 second. The life time of the F' center is found to be a few second at −10°C. These results are in qualitative agreement with Pick's observation.[10]

When the specimen was irradiated with the K band light of 443 ± 9 mμ at −100°C the F center resonance dropped in quite the same way as the irradiation of F light, as shown in the left half of Fig. 1. It suggests that the K band is the optical transition to one of the higher excited states of the F center, as was proposed by Mott[11] and was explained by Lüty.[3]

Until the previous year, the M center had been considered as the paramagnetic center. But the result of precise measurement of the *ESR* and optical absorption and their correlations confirmed non-magnetic nature of the M center.[12] This result is consistent with van Dooren, Haven[13] and Pick's model.[14]

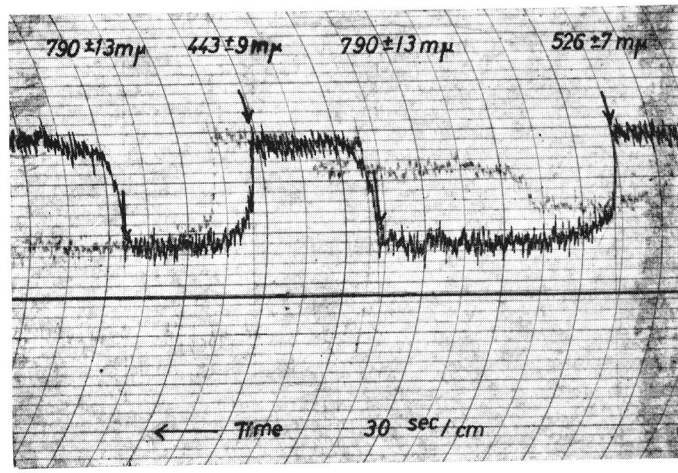

Fig. 1. The change of *ESR* signal by light irradiations in additively colored undoped *KCl* crystals at −100°C.

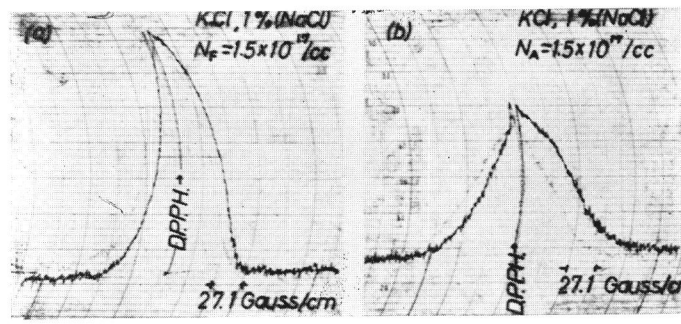

Fig. 2. Derivative traces of χ' in additively colored *KCl*:*Na* crystals; (*a*) the *F* center, (*b*) after creating the *A* center.

Na- or Li-doped KCl crystals

Derivatives of χ' signals before and after the creation of the sodium-*A* center are shown in Fig. 2 (the *A* center resonance was measured at −120°C, where it is stable, after creating the *A* center at −20°C and converting the *A'* center to the *A* center optically at −120°C). These traces were measured under the same condition. The half width of the *A* center resonance is 85±1 gauss and the area under the resonance signal remains almost constant without changing *g*-value in comparison with that of the *F* center.

The result can be analyzed qualitatively by the method used by Kip *et al.*[1] We analyzed the data for the *A* center on the following simplified assumptions: (1) The *A* center wave function extends over the six nearest neighbors (including five potassium ions and one sodium ion) and the twelve next nearest neighboring chlorine ions. (2) The *A* center wave function at the nuclei except the sodium is the same as that of the *F* center in *KCl*. Then one can easily obtain the *h.f.c.* (hyperfine coupling constant) of the sodium nucleus from the measured half-width to be 26.1 gauss. This value may be compared with 22.1 gauss which was obtained by Holton and Blum[15] as the *h.f.c.* of nearest neighboring sodium nucleus of an *F* center in *NaCl*. It may also be compared with the value of 28.4 gauss which is related to the *h.f.c.* of nearest neighboring potassium[15] by the ratio of the *h.f.c.* of free sodium and potassium atom.

The *B* center was also examined. The lithium-*B* center resonance shows about 63 gauss in half-width and the area under the resonance line remains almost constant without changing *g*-value in comparison with that of the *F* center. Preliminary result for the resonance of the sodium-*B* center shows

about 20% broadening without changing the g-value compared with that of the F center. Further study is necessary for the sodium-B center, since it appears together with the F and M center.

Sr-doped KCl crystals

The Z_2 band can be created at the expense of the F band when the additively colored *KCl*:*Sr* crystals are irradiated with the F light at any fixed temperature between 80°C and 160°C for a considerably long period. Although there is another treatment to obtain Z_2 band,[16] the subsequent results are independent of the method of treatment. When the colored *KCl* crystals, doped with 10^{-4} molar fraction of *Sr*, were quenched rapidly enough from the coloration temperature, they contained only F centers as shown in Fig. 3 (*a*). Curve (*b*) in Fig. 3 was obtained after the quenched sample was subjected to F light irradiation at 80°C. It must be noted that the new absorption band seems to appear on the shorter wave length side of the F band, which we tentatively call the Z_5 band.

The derivative traces of χ' in Fig. 4 (*a*) and (*b*) correspond to Fig. 3 (*a*) and (*b*), respectively. Trace (*b*) shows that the intensity is decreased in proportion to the optical density of the F center but significant change does not occur in the g-value, curve shape and its half-width in comparison with trace (*a*). It was confirmed that this relation is kept in various relative concentrations of F to Z_2 centers which were prepared at different temperatures. The *ESR* signal was completely recovered when the specimen containing Z_2 centers was subjected to a pulse annealing at 400°C. The fact was also ascertained in the χ'' trace under the non-adiabatic condition to avoid any spurious effect arising from the passage effects. Moreover, we could not detect any resonance associated with Z_2 centers in other spectral region ranging from g=1.4 to 2.4. Judging from these facts, one may conclude that the Z_2 center is non-magnetic.

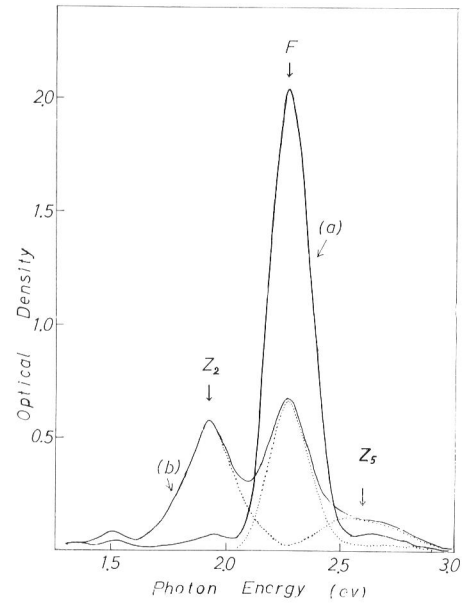

Fig. 3. Absorption spectra of *Sr*-doped *KCl* crystals measured at −180°C, (*a*) the virgin sample, (*b*) after exposed for 90 minutes to F light at 80°C.

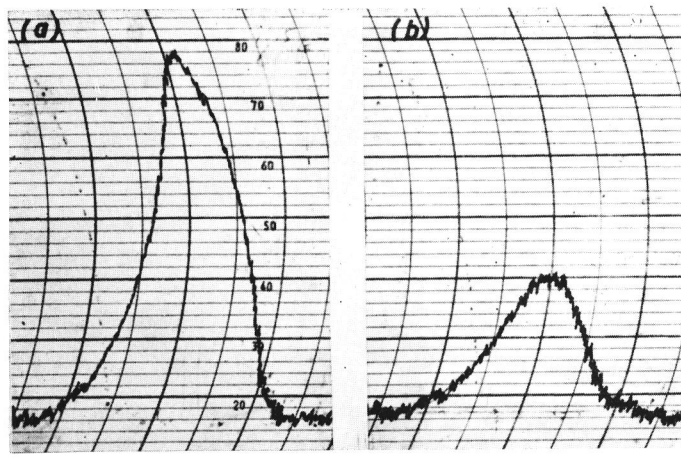

Fig. 4. Derivative of χ' measured at room temperature, corresponding to Fig. 3 (*a*) and (*b*), respectively.

When the specimen containing Z_2 centers (Fig. 5 (*a*)) is irradiated at −100°C with either the Z_2 band light or the F band light, the F' and the Z_3 band appear at the expense of the F, Z_2 and Z_5 bands as shown in Fig. 5 (*b*). The derivative traces of χ' in Fig. 6 (*a*) and (*b*) correspond to Fig. 5 (*a*) and (*b*), respectively. Trace (*b*) shows more than 10% narrowing (50±1 gauss) of the half-width and the area under the resonance line remains almost constant without changing the g-value in comparison with the trace (*a*) of the F center. Therefore, the trace (*b*) may be ascribed to the admixture of the F and the Z_3 center resonance. Assuming that roughly 30% of the trace (*b*) arises from the F center, one can obtain the half-width of the resonance line of Z_3 centers to be 47 gauss. At present we cannot reveal the exact half-width of the Z_3 center, since there is an ambiguous choice for the mixing degree of the F and Z_3 center.

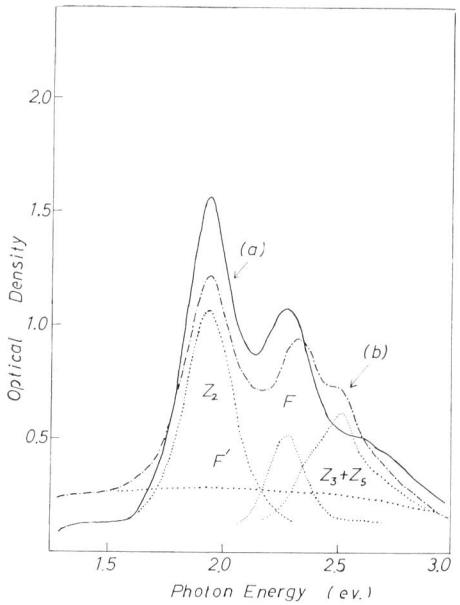

Fig. 5. Absorption spectra of *Sr*-doped *KCl* crystals measured at −180°C. (*a*) after exposed for 90 minutes to F light at 140°C; (*b*) subsequently the crystal was irradiated by Z_2 light at −100°C.

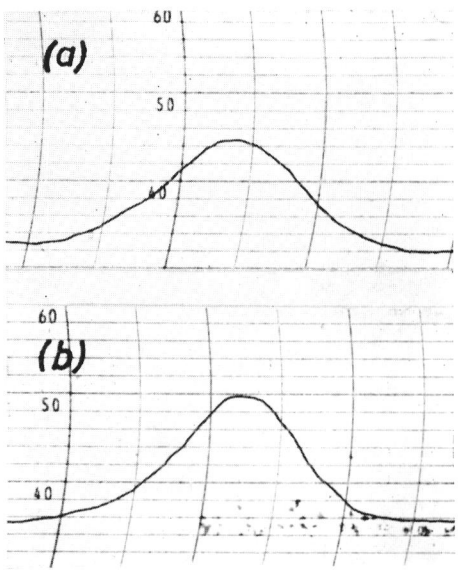

Fig. 6. Derivative traces of χ' corresponding to Fig. 5 (*a*) and (*b*), respectively. The trace (*a*) shows the contribution of F centers and the trace (*b*) may be considered as the admixture of F and Z_3 centers.

Up to now, two alternative models are proposed by Pick[17] and Seitz[18] for the Z_2 and Z_3 center. These models, however, are contradictory with our findings in view of the magnetic properties of the centers in question.

In order to explain our results, two alternative models may be proposed for the Z_2 center; one is a model in which a pair of divalent ions traps two electrons, and the other is a model in which a divalent ion, associated with a negative ion vacancy, traps two electrons (Fig. 7 (*a*) and (*b*)). The Z_3 center may be proposed to be an ionized Z_2 center.

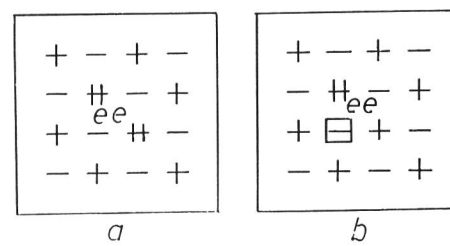

Fig. 7. Two possible models for a Z_2 center.

3. Conclusions

1. The non-magnetism of the F' and M center is confirmed. It seems that the K band is caused by the optical absorption to one of the higher excited states of the F center.

2. The paramagnetic nature of the sodium-A center is confirmed. From our results, it is evident that the NKL's model is correct.

3. As for the *Sr*-doped *KCl*, we have concluded the Z_2 center to be non-magnetic and

the Z_3 center to be paramagnetic. To explain our results, we tentatively proposed two possible models for each of them.

We wish to express our hearty thanks to Prof. M. Tomura and Dr. H. Otsuka for their kind discussion.

References

1 A. F. Kip, C. Kittel, R. A. Levy and A. M. Portis: Phys. Rev. **91** (1953) 1066.
2 K. Kojima, N. Nishimaki and T. Kojima: J. Phys. Soc. Japan **16** (1961) 2033.
3 F. Lüty: Z. Phys. **165** (1961) 17.
4 M. Ishiguro and E. Sugioka: Phys. Rev. **110** (1958) 1070.
5 R. L. Mieher: Phys. Rev. Letters **8** (1962) 362.
6 H. Pick: Z. Phys. **114** (1939) 127.
7 H. Kawamura and K. Ishiwatari: J. Phys. Soc. Japan **13** (1958) 574.
8 S. Miyamoto, S. Nakashima and H. Mizuno: J. Phys. Soc. Japan **17** (1962) 1076.
9 M. Weger: B. S. T. J. **39** (1960) 1013.
10 H. Pick: Ann. Phys. **31** (1938) 365.
11 N. F. Mott and R. W. Gurney: *Electronic Processes in Ionic Crystals*, Oxford University Press, London (1940) p. 114.
12 H. Ohkura and K. Murase: J. Phys. Soc. Japan **16** (1961) 2076.
13 C. Z. van Doorn and Y. Haven: Philips Res. Rep. **12** (1957) 309.
14 H. Pick: Z. Phys. **159** (1960) 69.
15 W. C. Holton and H. Blum: Phys. Rev. **125** (1962) 89.
16 G. Chiarotti, F. Fumi and L. Giulotto: *Defects in Crystalline Solids*, The Physical Society, London (1955) p. 317.
17 H. Pick: Same as reference 6; Ann. Phys. **35** (1939) 73.
18 F. Seitz: Phys. Rev. **83** (1951) 134.

DISCUSSION

Kojima, T.: Recently, we have discovered a new type of Z-centers in KBr which possesses [100]-symmetry and might be ascribed to an F'-center associated with a divalent ion.

Dryden, J. S.: I would like to ask the speaker if there is any difference in the Z-bands which appear if (a) the sample is stored at say 80°C for several hours and then irradiated with light in the F-band or (b) irradiated with light in the F-band immediately the sample attains this temperature (80°C).

Murase, K.: We have not performed such an experiment in detail. So far as our samples are concerned, there is no difference between the treatment (a) and (b). It is reported by Chiarotti *et al.* that the amount of the Z-bands depend greatly on the velocity with which the crystal was previously cooled from the temperature of coloration.