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Refractive-index change due to F color centers in KCl_xBr_{1-x} mixed crystals

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The refractive-index change due to F color centers in KCl_xBr_{1-x} mixed crystals was calculated from experimental absorption curves. The changes were of the same magnitude for all compositions. The binding of the F-center electron to its vacancy is discussed on the basis of these results.

I. INTRODUCTION

The invention of the color-center laser has greatly stimulated in recent years the study of different kinds of color centers in alkali halides. The color-center laser has provided, for instance, a device that at the moment can generate optical envelope solitons in fibers and has led to the realization of the soliton laser.[1] It has been suggested that an all-optical telecommunication system, demonstrated by Mollenauer and Smith[2] under laboratory conditions, can be based on the use of a color-center laser. In the light of such applications, therefore, it is perhaps not difficult to appreciate why there is an enthusiastic study going on of the uses of laser active color centers.

One group of colored alkali halides, mixed crystals, has not been submitted to such active investigation as those containing laser active color centers. Relatively few reports on their optical properties exist and those that do usually present measured or calculated absorption and emission data on these mixed crystals (see, e.g., Refs. 3–8). There are however, some basic properties of mixed alkali halides that provide us with more information about the color center. One such property is the wavelength-dependent refractive index, a subject untouched until now in connection with mixed alkali halides. In this paper we report on the refractive-index change of mixed KCl_xBr_{1-x} crystals of different compositions containing F color centers. Here x denotes the molar portion of KCl. On the basis of our calculations we have been able to draw some conclusions about the behavior of the F-center electron trapped in the anion vacancy.

II. EXPERIMENT AND RESULTS

In the present case we studied the refractive-index change due to F centers in KCl_xBr_{1-x} mixed crystals. The crystals were prepared by the Czochralski method in our laboratory and their composition was analyzed by taking Debye-Scherrer x-ray pictures from powered samples. Subsequently, the crystals were additively colored in an alkali-metal atmosphere and their absorption spectra were recorded at room temperature. Before refractive-index calculations were made, the absorption spectra were normalized to correspond to equal F-center concentrations in all the samples. Figure 1 presents the normalized absorption curves. Because the color-center concentration is proportional to the product of the maximum height and half-width of the absorption curves, the middle compositions have smaller heights as a result of the greater half-width behavior well known in the mixed crystals.

The calculation of the refractive-index change was based on the conjugate Fourier-series method introduced by King.[9,10] This method is an alternative to Kramers-Kronig dispersion relations. Its advantage is a shorter computing time compared to Kramers-Kronig calculations also done by computer. According to the King's model, the upper half of the complex angular-frequency plane is mapped conformally onto a unit disk as follows:

$$z=\frac{\hat{\omega}-i}{\hat{\omega}+i}\,, \tag{1}$$

where $\hat{\omega}$ is the complex angular frequency and i is the imaginary unit. The real axis $\mathrm{Re}\hat{\omega}$ is mapped onto the boundary of the unit disk. Now the refractive-index change $\Delta n = n - n_0$, where n_0 is the bulk value, and the

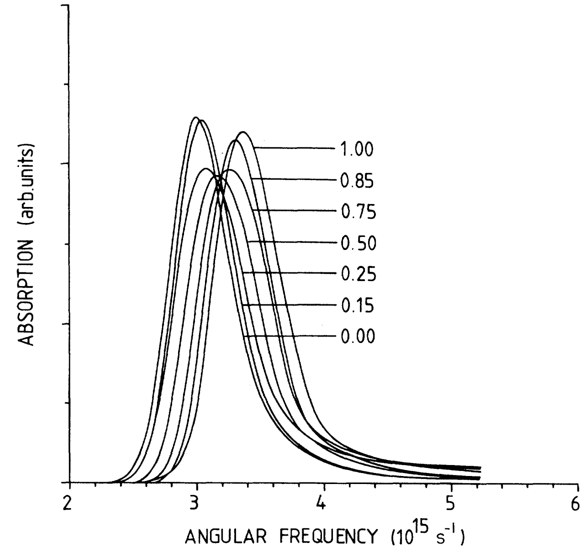

FIG. 1. Optical absorption as a function of angular frequency for KCl_xBr_{1-x} mixed crystals of different compositions containing equal concentrations of F centers. The x values for the curves are also indicated.

extinction coefficient k are given by the series expansions

$$\Delta n(\theta)=\frac{a_0}{2}+\sum_{m=1}^{\infty} a_m \cos(m\theta) \ , \tag{2a}$$

$$k(\theta)=-\sum_{m=1}^{\infty} a_m \sin(m\theta) \ , \tag{2b}$$

where $z=\exp(i\theta)$ and where the symmetry relations $k(\omega)=-k(-\omega)$ and $n(\omega)=n(-\omega)$ have been employed. The k values can be obtained from the absorption coefficients $\alpha(\omega)$ by using the well-known relation

$$k(\omega)=\frac{c\alpha(\omega)}{2\omega} \ . \tag{3}$$

Here c is the vacuum velocity of light. The idea is to calculate the coefficients α_m by fitting the extinction data to the series expansion of Eq. (2b). The refractive-index change can then be easily calculated with Eq. (2a). Our curves were calculated using the techniques proposed in Refs. 9 and 10. Before carrying out the calculations we first checked the consistence of the King's model with Kramers-Kronig relations using the theoretical extinction curves of Lorentzian and Gaussian shapes. In both cases the results obtained with King's model and Kramers-Kronig calculations agreed very well. Thus it was confirmed that King's model is applicable at least in the case of a single absorption band.

There is, however, one practical problem with the King's method as well as with the Kramers-Kronig relations. They both need information from the whole spectral range. This is impossible in the case of practical measurements. A good property of the King's method is the fact that it will give a relatively correct shape and magnitude for the refractive-index change even with limited band data. The main difficulty which we experienced was that the refractive-index change was not stabilized to a correct level. It was observed that the correct level can be obtained if the extinction coefficient has almost a zero value on the wings of spectrum. Fortunately, the present experimental data are favorable since they have asymptotic properties which give reliable results related to the refractive-index change. We do not discourage the use of King's model because the approximation of the wings beyond the measured data, not used here, is as valid for this method as when Kramers-Kronig relations are used.

It may be appreciated that the refractive-index change due to the F centers is related primarily to the real part of the complex electronic polarizability of the center. In turn, this polarizability is directly proportional to the induced dipole moment of the F center. The incident electric field of light causes the electron to be displaced from its equilibrium position. Furthermore, the polarizability is connected with the structure of the lattice around the electron. Compared to the ideal structure, the lattice is believed to relax around the F center.[11] Thus one is forced to assume that in the case of a mixed crystal the local irregularity of the lattice should influence the polarizability and accordingly also the refractive-index change. Thus from the refractive-index change we can obtain information about the polarizability and the displacement of the F-center electron. Furthermore, the displacement allows us to estimate how tightly the electron is bound to its vacancy under the influence of an external electric field. We can expect that no radical difference exists between a pure alkali halide and a KCl_xBr_{1-x} mixed crystal because the cations around the F-center electron are all similar in each case. A more enhanced effect is believed to arise in the case of different types of cations, for example, for $Na_xK_{1-x}Cl$ mixed crystals.

Figure 2 presents the refractive-index change for different compositions as a function of the angular frequency. First, we note that Fig. 2 confirms the result of Ref. 12, which states that KBr has a stronger refractive-index change due to the F centers than KCl in the case of equal F-center concentrations. This result has been observed to hold for these crystals if we assume that the local field experience by the F-center is either a Lorentzian or Onsager type.[13] Furthermore, we can easily state from Fig. 2 that, except for the somewhat greater change for KBr and its close compositions, all the values for the other samples are of the same magnitude. This tells us that the replacement of the anion in the crystal has a minor effect on the polarizability of the F-center electron. This occurs even though changing the lattice constant also changes the average excitation energy and thus accordingly the position of the absorption band. Thus the curve presenting the change in the refractive-index shifts as a function of composition x towards higher energies but has the same shape and magnitude for all compositions.

It is well known that if the F-center electron is treated as a particle in a box, its energy levels are inversely proportional to the square of the lattice constant.[14] In the present case, when we increase the amount of KCl in the composition we decrease the lattice constant. This results in a shift of the F band towards higher angular fre-

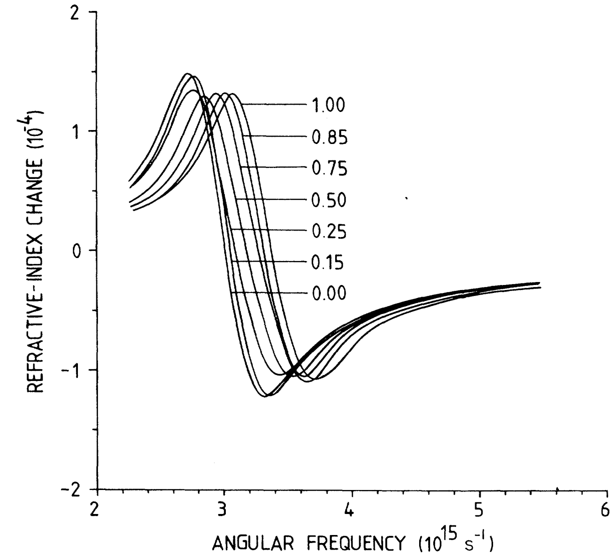

FIG. 2. Refractive-index change due to F centers in KCl_xBr_{1-x} mixed crystals as a function of angular frequency. The x values are as indicated.

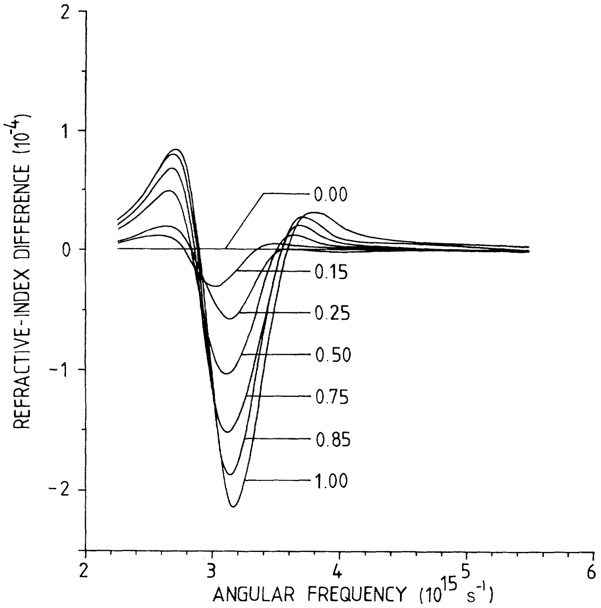

FIG. 3. Refractive-index differences for KCl_xBr_{1-x} mixed crystals as a function of angular frequency. The differences are calculated by comparing the refractive-index change of other compositions to that of pure KBr ($x=0.00$). The x values are as indicated.

quencies, as shown in Fig. 1. Simultaneously, when the KCl content is high enough, the only effect on Δn is the frequency shift in its range. Because the shape and magnitude of the change seem to stay almost constant, we can draw the rough conclusion that the F-center electron is not as tightly bound as x increases. Electron displacement of the same size can be found with both lower and higher values of x. Of course, the change in bulk crystal changes the effective field, but we assume that the bulk refractive index stays constant as a function of angular frequency for different x values, and the only contribution comes from F centers within the spectral range studied. Thus the shift of Δn is only due to the F centers.

Is there any possibility of comparing our different samples and their polarizabilities? Yes, there is. We may keep the refractive-index curve of pure KBr as a reference and subtract it from the curves of other compositions. The results are presented in Fig. 3. We observe that the difference curves, resembling those obtained for the birefringence of noncubic color centers,[15] have a strong minimum in the vicinity of the angular frequency 3.05×10^{15} s^{-1}. This minimum shifts slightly as a function of x towards higher frequencies. By comparing different compositions the strongest change is observed to occur in the region of anomalous dispersion of the samples where the displacement grows most strongly, a result that is not so clearly evident from Fig. 1.

III. DISCUSSION

We have studied the optical properties of mixed KCl_xBr_{1-x} crystals containing F color centers. It was observed that, starting from a relatively low value and increasing x to unity, a negligible effect on the magnitude of the wavelength-dependent refractive index of the crystals is obtained. The only clearly observable effect is the shift as a function of angular frequency which has its origin in the energy-level shift of F centers due to change in the size of the F-center vacancy. We propose that the F-center electron has, despite the change in the vacancy size, the same size of displacement under the incident electric field of the light wave. Decreasing the vacancy size keeps the electron relatively loosely bound.

The results were obtained with use of a model not having previously been applied for refractive-index calculations. Compared to the Kramers-Kronig relations, this model provides a relatively easy method for calculating refractive-index change. The method is used in conjunction with fast Fourier transforms. Some extrapolational errors may occur, but in the present case they remain negligible.

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