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Thermal Stability of Interstitial Halide Ions in Pure and Cl-Doped KBr†

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Studies were made of the effect of a Cl^- impurity on the formation of vacancies in KBr by x irradiation at low temperature and on the thermal annealing of the α band produced by x rays. It was found that both the annealing stage of the α band at 21°K and the sharp decrease of the formation efficiency of vacancies with temperature around 21°K are suppressed by the addition of the Cl^- impurity. The production of an "interstitial band" (5.36 eV) in pure and doped KBr was also studied. It is suggested that in doped KBr the Br^- interstitials are replaced by more stable Cl^- interstitials and that this replacement accounts for the higher formation efficiency above 21°K. The distance of the ejection of a Br^- interstitial by x ray is estimated to be about 10 atomic spacings.

I. INTRODUCTION

ANY quantitative discussion of radiation effects in the alkali halides at low temperatures must consider the formation of the α center as well as the F center. Although the efficiency of formation of F centers by x-irradiation has been shown[1] to be independent of impurities at low temperature, Bauser and Lüty[2] have observed that the formation efficiency of α centers in Cl-doped KBr at 90°K is as much as three times higher than that of pure KBr. They have proposed that either the Cl^- site accepts more of the excitation energy created by the x irradiation or that the Cl^- interstitial is more stable than the Br^- interstitial and hence reduces the number of vacancies destroyed by recombination. Gebhardt,[3] in measurements of the thermal resistivity of KBr containing α centers, has shown that the interstitials anneal in the region of 20°K. Studies[4] of the thermal annealing of x-ray-produced α centers at low temperatures indicate that Br^- interstitials become mobile at 21°K with an activation energy of 0.06 eV for random migration. This value compares reasonably well with the theoretical value[5] of 0.19 eV for the activation energy for interstitialcy migration of Br^- and is in sharp disagreement with the value of 2.21 eV for interstitial migration. So far, no experimental results have been published on the migration energy of interstitials in KBr doped with Cl^-; however, Seitz[6] has suggested (in connection with his model of the V_1 center) that Cl^- interstitials in KBr are more stable, once formed, than the corresponding Br^- interstitialcy.

As already pointed out by the present authors,[4] the annealing of a band at 5.36 eV (230 mμ) formed by x irradiation at 16°K parallels the recombination of the vacancies and interstitial ions. It was suggested that this band was due to the presence of interstitial bromine ions. This has recently received elegant confirmation by Kurz and Gebhardt[7] who observed the simultaneous annealing of this optical absorption and the thermal resistance due to the interstitial ion. An estimate[8] of the energy necessary to take an electron from an interstitial halide ion into the conduction band is in reasonable agreement with the observed optical absorption of the interstitial band. The formation efficiency of the α band was measured in a wide range of temperature by Rüchardt,[9] and a sharp drop of the efficiency was observed around 20°K at which the free migration of Br^- interstitials takes place. It is therefore of interest to study the migration of interstitials in Cl^--doped KBr and its relation to the formation efficiency of vacancies by low-temperature x irradiation.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

Most of the experimental procedures are the same as previously described.[4] The pure specimens were obtained from an ingot purchased from the Harshaw Chemical Company, and the doped specimens were obtained from ingots grown at Professor A. Smakula's laboratory. Optical absorption was measured by a Cary 14R spectrophotometer. Specimens were irradiated by 100-kV 10-mA x rays from a tungsten-target constant-potential tube filtered through 3-mm Al and 1.5-mm KBr. The isochronal experiments were made by measuring the absorption coefficient at the α-band maximum while the specimens are warmed. No corrections were made for the change of the half-width of the α band with temperature, since over the temperature range employed this will not introduce more than a 10% error in the concentration of α centers.

Figure 1 shows the isochronal annealing of α centers in Harshaw KBr and KBr doped both with 1-mol% and with 8-mol% Cl. It is clear from Fig. 1 that the sharp annealing stage of the α center at 21°K (corresponding to the motion of Br^- interstitialcy[4]) is completely suppressed by 8-mol% Cl. In KBr doped with

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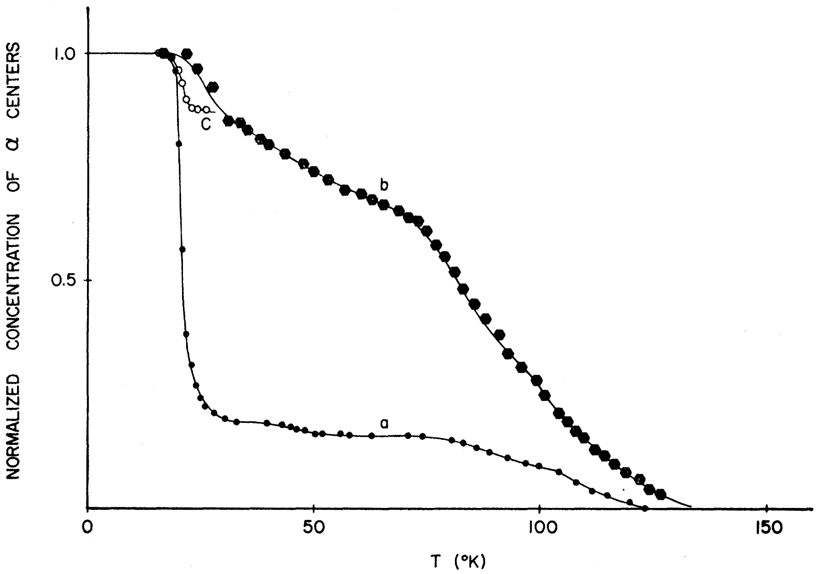

FIG. 1. Annealing curves of α centers formed by x irradiation at 16°K in Harshaw KBr (curve a), KBr with 8-mol% Cl (curve b), and KBr with 1-mol% Cl (curve c).

1-mol% Cl, on the other hand, the sharp decrease of α band at this annealing stage exists but is smaller by a factor of 6 as compared to pure KBr. The complex annealing pattern at higher temperatures, especially in doped specimens, probably corresponds to the migration of Cl^- interstitials in KBr, although no detailed analysis of this annealing spectrum has been made. A rough estimate, using the isochronal annealing curve, shows that the activation energy for the annealing stage at circa 110°K is about 0.3 eV.

Figure 2 shows a comparison of the change of optical-absorption curves due to x irradiation for pure and for KBr doped with 8-mol% Cl at both 16 and 22°K. The 5.36-eV band does not appear in pure KBr at 22°K nor in KBr doped with 8-mol% Cl even at 16°K. The magnitude of this band in KBr doped with 1-mol% Cl is about one-third of that in pure KBr.

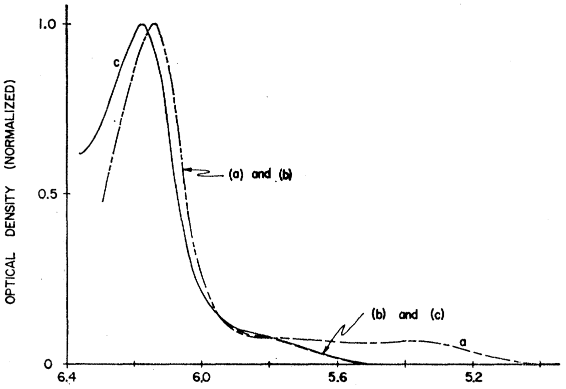

FIG. 2. Ultraviolet optical-abosorption curves of KBr. (a) Harshaw KBr x irradiated at 16°K, (b) Harshaw KBr x irradiated at 22°K, (c) KBr (8-mol% Cl) x irradiated at 16°K.

Figure 3 shows the formation of vacancies as a function of time at both 16 and 22°K for pure KBr and for KBr doped with 1- and 8-mol% Cl. To obtain the total number of vacancies by adding the numbers of α centers and F centers, the ratio of the oscillator strength

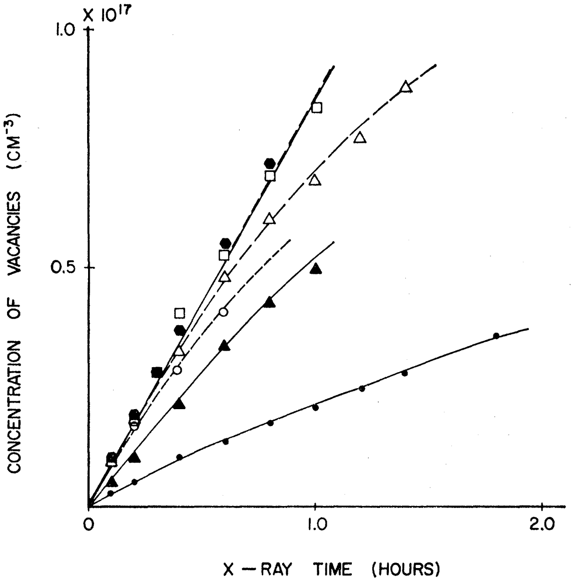

FIG. 3. Formation of vacancies by x irradiation in pure and in Cl-doped KBr at low temperatures.

Symbol	Temperature of irradiation (°K)	Crystal
Open circle	16	Harshaw KBr
Filled circle	22	Harshaw KBr
Open triangle	16	KBr (1-mol% Cl)
Closed triangle	22	KBr (1-mol% Cl)
Square	16	KBr (8-mol% Cl)
Hexagon	22	KBr (8-mol% Cl)

of an α center to that of an F center was taken to be[10] 1.31 and the half-width of both absorption bands was taken to be the same.[11] Two significant features should be noted: (1) At 16°K, the Cl^- impurity does not affect the initial rate of formation of vacancies; and (2) the formation efficiency at 22°K is lower than that at 16°K and, as the concentration of Cl^- impurity increases, the difference in the rate of formation of vacancies at the two irradiation temperatures decreases.

III. DISCUSSION

The results of the above thermal-annealing experiments suggest that the recombination between Br^- Frenkel pairs is reduced by an addition of Cl^- to the KBr lattice. A correlation between the efficiency of vacancy formation and the stability of the interstitial ions is found to exist. Below 16°K, where previous experiments have shown that the Br^- Frenkel pairs are stable, the formation efficiency is not affected by the addition of Cl^- ions to the lattice. The decrease in formation efficiency observed in pure specimens as the temperature increases above 21°K is found to be less in specimens containing more Cl^- impurity.

As expected, the Cl^- interstitials in KBr are more stable than Br^- interstitials and require a higher activation energy for interstitialcy migration. These results suggest that the Br^- interstitials are replaced by Cl^- interstitials either (1) during the creation process of the Frenkel pairs or (2) during the recombination of the created Frenkel pairs. A choice between these two possibilities was made by observing the 5.36-eV band which has been assigned to the Br^- interstitials. This band was not observed[12] in KBr doped with 8-mol% Cl and x-rayed at 16°K, and it was suppressed considerably in KBr doped with 1-mol% Cl^-. It is therefore suggested that in the crystal with 8-mol% Cl^- impurity the Br^- interstitial is replaced by a Cl^- interstitial during the vacancy-*creation* process, and that the enhanced stability of the Frenkel pairs in this material is due to the difficulty of the Cl^- initiating the interstitialcy recombination path, rather than its acting as a trap for a moving Br^- interstitialcy. Thus in 8-mol%-doped KBr most of the Frenkel pairs will be of the mixed form (Br^- vacancy+Cl^- interstitial) and be stable above 21°K. In the 1-mol% Cl^- crystal the enhanced vacancy-formation efficiency must be due, in large part, to a similar creation of mixed (Br^- vacancy Cl^- impurity) Frenkel pairs. In this case, however, normal Br^- Frenkel pairs also exist, and during the recombination process by interstitialcy migration some of them may be stopped by an encounter with a Cl^- impurity. This additional process would account for the smaller amount of recombination observed at 21°K than that expected from the difference in the formation efficiency between the doped and the pure material. Thus, in general, only if the Br^- interstitial is replaced by a Cl^- (or some other impurity) or trapped at a lattice defect will a Frenkel pair be stable above 21°K. It is reasonable to conclude, therefore, that the stability of interstitial ions is the primary factor determining the initial efficiency of vacancy formation. It appears that the increased efficiency of α-center formation at 90°K observed by Bauser and Lüty[2] is due to the thermal stability of the Cl^- interstitial rather than to the localization of excitation energy at the substitutional Cl^-. If the latter were true, the Cl^- impurity should have enhanced the formation efficiency of α centers at 16°K.

If one assumes that the interstitial Br^- ions are replaced by Cl^- ions during the formation process of a Frenkel pair, an estimate of the distance of ejection of Br^- interstitials can be obtained. The probability that an ejected Br^- ion meets a Cl^- impurity while traveling a distance of j lattice parameters is $p_j=[1-\exp(-znj/N)]$, where z is the number of surrounding ions which can interact with the ejected interstitial while it travels one-unit-lattice distance, n is the concentration of the Cl impurity, and N is the number of unit cells per unit volume. In KBr doped with 0.1-mol% Cl^-, the decrease of the efficiency on going from 16 to 21°K is roughly half of that in pure KBr. Thus, putting $p_j=0.5$ one obtains $jz=70$. The value of z depends on the mechanism of migration of the ejected ions. It is reasonable to assume that the Br^- interstitial replaces a substitutional Cl^- when the Cl^- is one of the nearest neighbors of the moving Br^- interstitial. The value of z is thus expected to be around 6, giving j about 10. This value of j agrees with the fact that no decrease of the efficiency of vacancy formation is observed in KBr doped with 8-mol% Cl as 21°K is passed. This estimate of j is also consistent with the fact that most vacancies which disappear at the 21°K annealing stage are α centers. The presence of a charged interstitial within about 10 lattice parameters from the vacancy should be sufficient to prevent the vacancy from capturing an electron and becoming an F center.[13]

In view of the above discussion, it is necessary to consider the nature of the complementary defects of α centers in pure KBr above 21°K, since it was concluded that at these temperatures the Br^- interstitials are unstable. Experiment shows that with increasing irradiation dose the magnitude of the annealing stage of the α band at temperatures higher than 21°K in pure

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[10] R. Onaka and I. Fujita, J. Quant. Spectry. Radiative Transfer **2**, 599 (1962).

[11] The half-width of the α band at 21°K was about 0.2 eV (see Ref. 5), with an accuracy of about 10% because of overlap with a γ band on the short-wavelength side. This error, however, is not very important for the calculation of concentration of vacancies because the height of the F band is about 1/5 the height of the α band.

[12] Using the experimentally determined shift in the γ band observed by Lüty and Zizelmann [Solid State Commun. **2**, 179 (1964)] any band due to the Cl^- interstitial would be expected to be on the short-wavelength side of the 5.4-eV band and would probably overlap the α band or a band at 5.8 eV. Its expected magnitude would make its detection extremely difficult.

[13] F. Lüty, Z. Physik **153**, 247 (1958).

KBr increased more rapidly than that of the 21°K annealing stage. This result suggests that heavier irradiations produce more stable complex forms of interstitial halide ions and that these account for the occurrence of higher temperature annealing stages. It is interesting to note that the concentration of the isolated halide interstitial atoms (the H centers) saturates as a function of radiation dose but that the growth of the H'[14] center is a linear function of the F-center concentration.

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Note added in proof. The authors are grateful to Dr. F. Lüty for bringing to their attention the work of U. Strähle (Diplom, Stuttgart, 1963) in which similar annealing of the α center in Cl-doped KBr is discussed together with an experimental determination of the efficiency of vacancy formation between liquid-helium temperature and 100°K.

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Far-Infrared Magnetic Resonance in NiF_2

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Measurements of the far-infrared transmission of the canted-spin antiferromagnet NiF_2 using the technique of Fourier-transform spectroscopy are described. Resonant absorptions were found at $\nu_1 = 3.33 \pm 0.05$ cm^{-1} and $\nu_2 = 31.14 \pm 0.1$ cm^{-1} with applied field $H=0$ and temperature $T \approx 0$. Using the resonance relations derived by Joenk and Bozorth from Moriya's model, these give anisotropy and exchange parameters $E=1.66$ cm^{-1} and $8JD=482.2$ cm^{-2}. A good fit is obtained to the measured magnetic-field dependence of both modes for $g_\perp = 2.35$ which, along with the measured perpendicular susceptibility, gives $8J=125$ cm^{-1} and $D=3.86$ cm^{-1}. The temperature dependence of ν_2 was measured between 1.2 and 65°K ($T_N = 73.2$°K) and is found to be in agreement with the Zener theory when the temperature dependence of the sublattice magnetization is estimated from neutron-diffraction intensity measurements. The linewidth and strength of mode 2 were also measured as a function of T, and are discussed qualitatively.

I. INTRODUCTION

THE magnetic properties of the iron-group difluorides MnF_2, FeF_2, CoF_2, and NiF_2 have been studied extensively from both an experimental and a theoretical point of view. All these compounds have the rutile crystal structure shown in Fig. 1, and have Néel temperatures T_N between 35 and 75°K, below which magnetic ordering takes place. Susceptibility measurements on MnF_2, FeF_2, and CoF_2 show that the ordering is antiferromagnetic, and neutron-diffraction experiments indicate that the spins point along the $\pm z$ axis.[1] Torque measurements by Mataresse and Stout[2] show that NiF_2, on the other hand, has a weak ferromagnetic moment along a [100] direction. The existence of this moment was explained by Alikhanov,[3] from neutron-diffraction experiments, and by Moriya,[4] from a theoretical interpretation of the torque measurements, in terms of the canted two-sublattice magnetic structure shown in Fig. 2. As was pointed out by Dzialoshinski,[5] and calculated quantitatively by Moriya,[6] there are, in general, two interactions which can cause canted-spin systems. Of these, the antisymmetric exchange coupling,

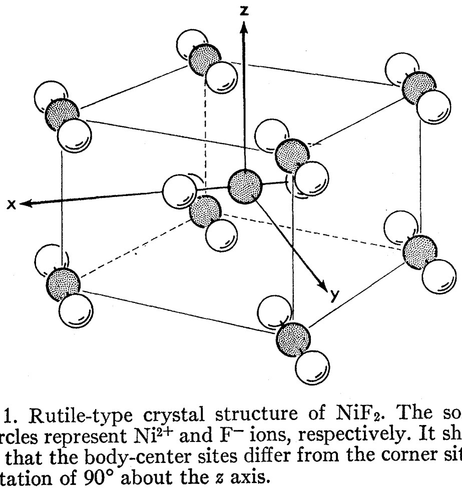

FIG. 1. Rutile-type crystal structure of NiF_2. The solid and open circles represent Ni^{2+} and F^- ions, respectively. It should be noticed that the body-center sites differ from the corner sites only by a rotation of 90° about the z axis.

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