

Bismuth centers in alkali halides

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Bismuth enters into the alkali halide lattice in its trivalent and/or divalent state if it is introduced by diffusion of bismuth vapors at appropriate temperatures. In its trivalent state its ground state is 1S_0 and transitions from this level to the 3P_1 , 3P_2 , and 1P_1 states are the well known *A*, *B*, *C* bands of the ns^2 configuration. Such bands are observed in NaCl, KCl, KBr, and RbCl crystals doped with bismuth. In its divalent state bismuth has one intense band at ~ 390 nm. On radiation damage or additive coloration it is possible to reduce the valence state, and by controlled experiments it has thus been possible to introduce and study the properties of Bi^{+++} , Bi^{++} , Bi^+ , Bi^0 , and even colloids of atomic bismuth in these crystals. When the colloids of bismuth are formed, the centers give the characteristic optical absorption band in the uv region (~ 275 nm), give enhanced conductivity which can be attributed to thermionic emission of electrons from bismuth colloidal particles, and give characteristic conduction-electron spin-resonance signals (18 G in KBr). These features persist till the melting point of the crystal and their intensity is a function of concentration. Electron microscopic studies lend support to this interpretation.

I. INTRODUCTION

Most of the earlier work in impurity-doped alkali halide crystals has been confined to divalent impurities.¹ In cases where rare-earth ions have been incorporated² in their trivalent state several interesting features were observed, particularly in the transport phenomena exhibited by these crystals. Certain impurities such as antimony could be introduced³ into the crystal in its divalent and trivalent states by diffusion but the concentration of these states could not be controlled independently. In an attempt to introduce an impurity which could be added in controlled concentrations to the crystal in either its divalent or trivalent state, it was found that bismuth was an ideal case. It has already been reported⁴ that the diffusion coefficients of bismuth in its divalent and trivalent states were such that at higher temperatures the divalent bismuth is predominant while at lower temperatures trivalent bismuth is predominant. It was therefore thought that by controlled experiments it would be possible to introduce a predominance of one state or the other. After thus introducing the impurity in its trivalent and/or divalent states the valence states of the impurities have been modified by subjecting the crystal to radiation damage or additive coloration. In this process it was possible to form Bi^+ , Bi^0 , and aggregates of Bi^0 centers in the crystal. To investigate these centers a set of correlated experiments such as conductivity, dielectric loss, optical absorption, and ESR have been used. Besides these tools electron-microscope pictures have been taken in an attempt to directly observe the colloidal formation.

II. EXPERIMENTAL METHODS

Single crystals of NaCl, KCl, KBr, KI, and RbCl were grown by Kyropoulos technique and the impurity was diffused by heating the crystals in vapors of $BiCl_3$, or bismuth metal. Optical-absorption measurements were made by using Cary-14 spectrophotometer. ESR measurements were made by a Varian V-4502-12 EPR spectrophotometer and electron microscope pictures were taken by using a Elmiskop 1A of Siemens. Conductivity measurements were made by measuring the resistance of a sample subjected to 100 dc V. A GR 1644 megohm bridge was used for resistance measurements. The voltage was applied to the crystal faces for a short time to ensure that there were no polarization effects. Dielectric-loss measurements were made by using a GR 1615-A capacitance bridge combined with a GR 1311-A audio oscillator. For dielectric-loss measurements the temperatures of the crystals were controlled by a Phillips "Plastomatic" Temperature Controller.

III. RESULTS AND DISCUSSIONS

A. Uncolored crystals

1. Optical absorption

The results will be discussed with reference to data obtained by diffusion at three different temperatures, 400°C for crystal *A*, 500°C for crystal *B*, and 600°C for crystal *C*. If bismuth is present in its trivalent state the ion has an ns^2 configuration and *A*, *B*, and *C* bands are to be observed,⁵⁻⁷ and if it is in its divalent state, a single band is to be expected. As results presented will show, both Bi^{+++} and Bi^{++} centers

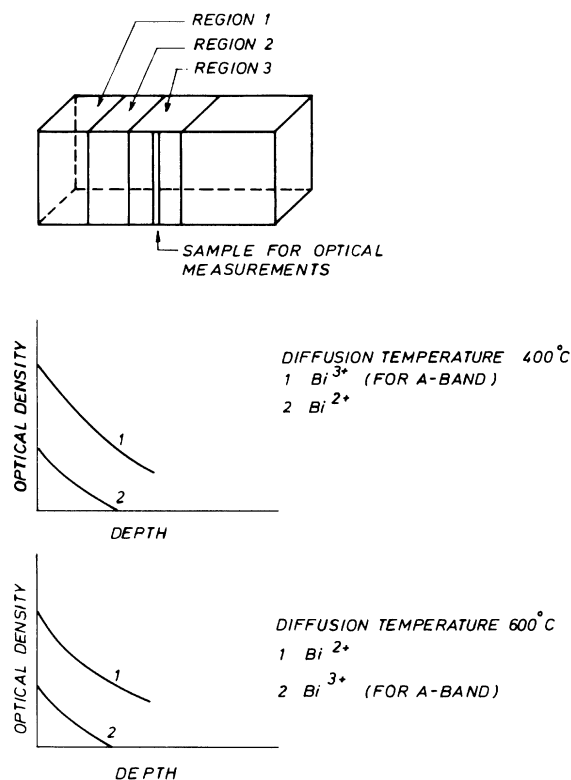


FIG. 1. Schematic representation of penetration profiles of optical bands found by diffusion of bismuth at various temperatures.

are obtained for different temperatures of diffusion. In the case of crystal A, a predominance of Bi^{3+} is observed in all regions of the crystal (Fig. 1). The concentration of bismuth varied as we progressed from the surface to the interior. Figure 1 shows different regions of a crystal into which bismuth is diffused and a schematic representation of penetration profiles. Figure 2 shows a typical optical-absorption spectrum in the interior of an NaCl crystal into which bismuth was diffused. It can be seen that three prominent

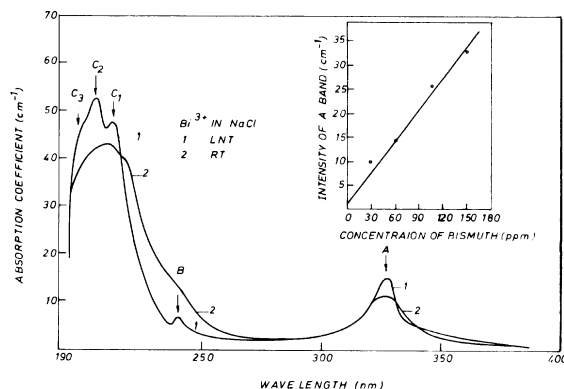


FIG. 2. Optical absorption of Bi^{3+} centers in NaCl. Diffusion of bismuth at 400°C . Inset shows concentration of bismuth vs intensity of A band. Sample from interior of the crystal.

bands—in order of increasing energy A, B, and C—are observed. The C band also shows a structure with three components marked C_1 , C_2 , and C_3 . This spectrum is characteristic of an ion which has an ns^2 configuration, and the intensity of the three bands either increases or decreases together. This implies that all three bands belong to the same center. These bands are attributed to Bi^{3+} . The inset of Fig. 2 shows a plot of intensity of an optical band (A band) as a function of concentration of bismuth. Such bands are observed in different alkali halides, after diffusion of bismuth at a temperature $\sim 400^\circ\text{C}$. Results obtained in the cases of NaCl, KCl, KBr, KI and RbCl are shown in Table I. These results show that only trivalent bismuth is present in the interior of a crystal. No other bands are present, and hence other valence states can possibly be ruled out.

If, however, diffusion is done at 600°C , different results are obtained. In the interior of the crystal (region 3 of Fig. 1) no bands which can be ascribed to Bi^{3+} are found but a new band is

TABLE I. Optical bands due to Bi^{3+} and Bi^{2+} in alkali halide crystals.

Crystal	Lattice constant (Å)	Bi^{3+} band							Bi^{2+} band			
		A band (nm)		B band (nm)	C band (nm)			Peak position (nm)		Half-width (eV)		
		RT ^a	LNT ^b	LNT	C_1	C_2	C_3	RT	LNT	RT	LNT	
NaCl	5.628	328	325	240	212	205	~ 198	335	328	0.29	0.26	
KCl	6.28	330	325	244	212	207	201	345	338	0.27	0.26	
KBr	6.59	370	364	275	233	222	216	390	380	0.24	0.22	
KI	7.052	380	375	280	240	231	223	400	395	0.23	0.20	
RbCl	6.54	360	356	270	228	220	210	375	360	0.24	0.19	

^aRoom temperature.

^bLiquid-nitrogen temperature.

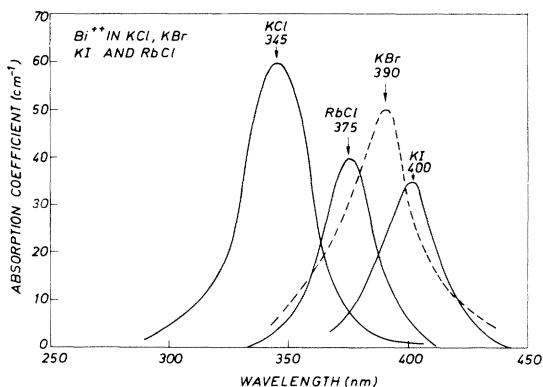


FIG. 3. Bi^{**} optical absorption at room temperature in different crystals. Diffusion at 600°C for 48 h for all crystals.

observed. In KCl, this band is found at 345 nm (Fig. 3). There are no other bands which seem to be associated with this optical band. The band, however, is a function of bismuth concentration. Thus the band at 345 nm must be ascribed to a different valence state of bismuth. The most likely valence state is the divalent one, and support for this comes from conductivity and dielectric loss (results reported below). A similar optical absorption band is observed in other alkali halides, and Table I also gives details of such bands. Figure 3 shows the bands observed in KCl, RbCl, KBr, and KI. These results show that if diffusion is performed at higher temperature, Bi^{**} is predominantly present inside the lattice.

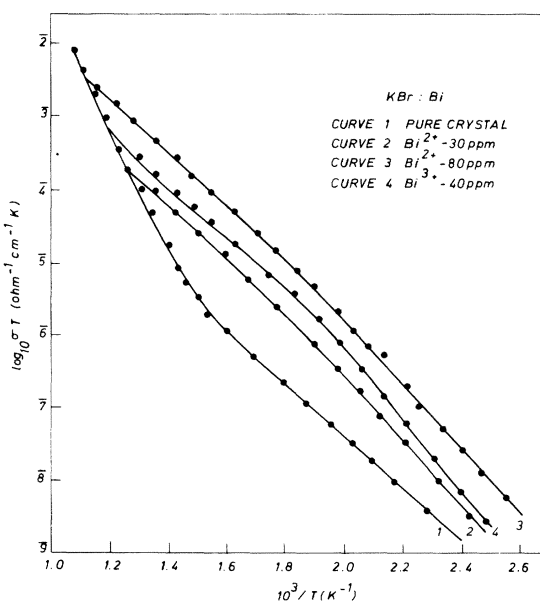


FIG. 4. $\log_{10} \sigma T - 1000/T$ plots for KBr crystal containing bismuth.

The results shown in Fig. 3 are all for diffusion at 600°C for 48 h, and it can be seen that the maximum concentration is in KCl. Thus the diffusion coefficient is largest in KCl. In the outer regions, or if diffusion is performed at intermediate temperatures both states are simultaneously present.

2. Ionic conductivity

Figure 4 shows a plot of $\log_{10} \sigma T$ vs $1000/T$ for a KBr crystal in which curve 4 is for a crystal containing 40 ppm bismuth impurity in its trivalent state. An analysis of the different regions of the curves gives $W_s = 1.80$, $E_c = 0.70$, and $W_a = 0.62$ eV, where W_s is the energy of formation of Schottky defects, E_c is the energy of migration of a cation vacancy, and W_a is the free energy of association of the impurity ion with the cation vacancies. Figure 4 also shows the conductivity of KBr containing divalent bismuth. The W_a value obtained now is different, and this once again supports the interpretation given on the basis of optical absorption studies. The value for W_a obtained is 0.62 eV and is much higher than the normally reported value for a divalent impurity⁸ with a bound vacancy. The explanation for this high W_a has to be sought in the trivalent nature of the impurity, and the result can be interpreted as the binding energy of the trivalent impurity with one vacancy. The other vacancy required for charge compensation—with bismuth occupying a substitutional site—is either far away or bound with much less energy. The data obtained from analyzing the slopes of the curves in Fig. 4 is summarized in Table II.

Conductivity measurements on crystals obtained by diffusion at 600°C give different results. Corresponding optical absorption measurements have shown the existence of bismuth in its divalent state only. Curve 2 in Fig. 4 shows results of conductivity studies in a KBr crystal containing Bi^{**} (30 ppm), and an analysis of the curves gives $W_s = 1.80$, $E_c = 0.7$, and $W_a = 0.36$ eV. It can be seen that if the concentration is increased to 80 ppm (curve 3), the third and second regions are enhanced but the same slope is maintained.

TABLE II. Energy parameters (in eV) obtained from conductivity measurements of Bi^{***} and Bi^{**} centers in alkali halide crystals.

Crystal	W_s	E_c	W_a (Bi^{***})	W_a (Bi^{**})
NaCl	2.2	0.80	0.64	0.32
KCl	2.16	0.80	0.66	0.36
KBr	1.80	0.70	0.62	0.36
KI	1.72	0.70	0.60	0.32
RbCl	1.85	0.85	0.72	0.58

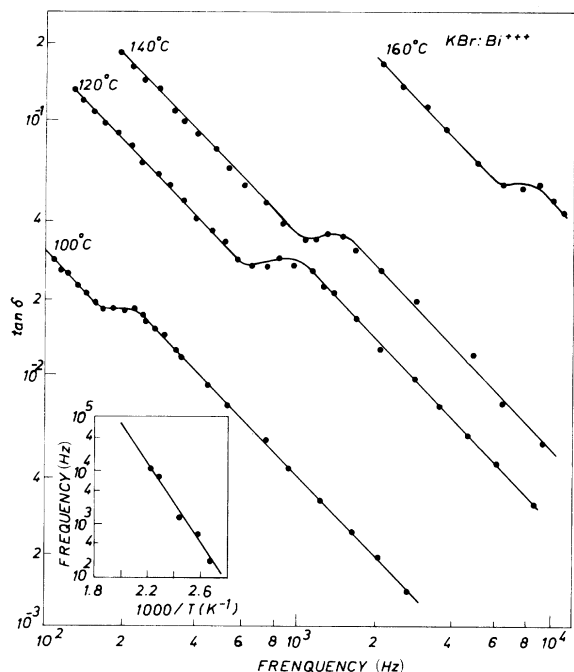


FIG. 5. $\tan\delta$ -vs-frequency plots for KBr crystal containing trivalent bismuth. Inset shows f_{\max} vs $1000/T$.

The value for W_a of 0.36 eV suggests a divalent impurity with a bound vacancy. Similar results obtained in crystals of other types give binding energies in the case of impurity-vacancy complexes, and the data is summarized in Table II.

For samples into which diffusion is done at an intermediate temperature (500 °C) the value of W_a obtained is not the same as for a sample obtained from the outer region of the crystal, and it lies between 0.3 and 0.65 eV depending on the position from where the sample is obtained and the temperature at which diffusion is performed. Thus the essential information obtained from conductivity is that the impurity has a binding energy of ~ 0.62 eV if it is in the trivalent state and ~ 0.36 eV if it is in the divalent state.

3. Dielectric loss

Figure 5 shows dielectric-loss results in the case of a KBr crystal containing 30 ppm of the impurity in its trivalent state. Curves 1, 2, 3, and 4 show $\log_{10} \tan\delta$ vs \log_{10} (frequency isothermals) obtained at 100, 120, 140, and 160 °C respectively. Each curve shows only one loss peak, and the peak frequency f_m shifts to higher frequencies as the temperature is increased. Measurements made on crystals of higher concentration confirm that the loss peak is indeed due to the presence of the impurity. These results indicate that as the temperature is increased, higher frequencies of the ac field are required to orient

the dipoles in order to get relaxation losses. The inset of Fig. 5 shows the plot of $\log_{10} f_m$ vs $1000/T$, where T is the temperature of measurement of the dielectric-loss factor in °K. Since the plot gives a straight line, an equation of the type $f_m = f_0 e^{-E/KT}$ can be used to describe it, where f_0 is the frequency factor which is related to the time constant τ_0 of the free vibration of the lattice and E is the activation energy for the jump of a cation vacancy bound to the impurity ion. The slope and the intercept of the straight line, respectively, give the values of the activation energy for migration of a bound cation vacancy as 0.82 eV and of f_0 as $0.85 \times 10^{12} \text{ sec}^{-1}$. Similar dielectric-loss results are obtained in the case of RbCl and KCl crystals as well, and the data is tabulated in Table III.

If the measurements are made on crystals in which diffusion is performed at 600 °C and results analyzed, an activation energy of 0.63 eV is obtained. This is typical of a divalent impurity-vacancy complex and is interpreted as the activation energy for the reorientation of a divalent impurity-vacancy dipole. The significant aspect of these studies is the fact that when the impurity is in the trivalent state only one loss peak is observed. This is indicative of the fact that only one type of relaxing dipole is present, and this can be interpreted by postulating only one bound vacancy. The higher activation energy is to be expected because of higher binding energies. The width of the Debye loss peak is not unreasonably large, and hence one cannot think of two types of relaxing dipoles with nearly the same frequencies.

Dielectric-loss results for samples in which diffusion is performed at 500 °C are more complex and are not amenable to easy interpretation. They give more than one loss peak, and the loss peaks themselves are broadened.

TABLE III. Activation energies and preexponential frequency factor of dielectric-loss factor observed in bismuth-doped alkali halides.

Crystal	Activation energy (eV)	Frequency factor (sec^{-1})
NaCl : Bi ⁺⁺⁺	0.8	1.2×10^{12}
NaCl : Bi ⁺⁺	0.7	0.9×10^{12}
KCl : Bi ⁺⁺⁺	0.83	1.8×10^{13}
KCl : Bi ⁺⁺	0.66	1.4×10^{12}
KBr : Bi ⁺⁺⁺	0.82	0.85×10^{12}
KBr : Bi ⁺⁺	0.63	1.83×10^{13}
KI : Bi ⁺⁺⁺	0.82	1.35×10^{12}
KI : Bi ⁺⁺	0.61	0.98×10^{13}
RbCl : Bi ⁺⁺⁺	0.79	1.5×10^{12}
RbCl : Bi ⁺⁺	0.70	1.3×10^{12}

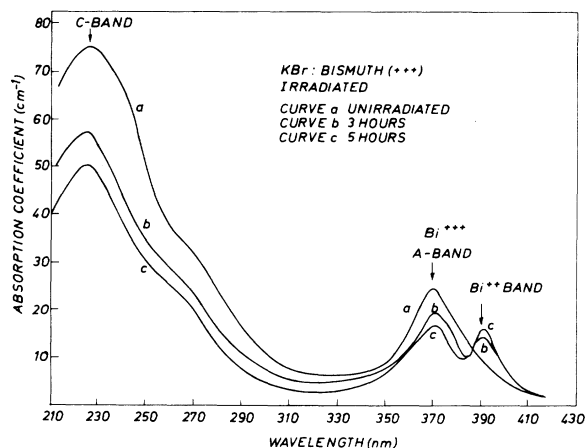


FIG. 6. Optical-absorption bands in KBr crystals containing trivalent and x-irradiated bismuth.

4. Irradiated crystals

We now discuss results of radiation damage in bismuth-doped alkali halides. Curve (a) in Fig. 6 shows an optical spectrum of a KBr crystal containing Bi^{3+} . Curve (b) shows the spectrum obtained on irradiating the crystal for 3 h, while curve (c) shows the spectrum obtained after 5 h of irradiation. It can be seen that after a rapid initial decay of the Bi^{3+} optical band, there is a tendency to saturate. The reduction of Bi^{3+} is accompanied by a rise in the Bi^{2+} optical band. A suppression of the F band is also observed, but it is not shown in Fig. 6. Prolonged irradiation does not seem to produce complete conversion of the valence state. The conversion of bismuth from a trivalent state to a divalent state is limited to about 30%. Similar conversion is obtained in other crystals as well. Even after 24 h of x-irradiation no monovalent bismuth was observed.

In the case of KBr crystals containing bismuth in its divalent state, irradiation reduces the Bi^{2+} optical band, and a new band is found at 310 nm. This band increases either with time of irradiation or if crystals containing a larger concentration of the impurity are used. The crystals containing Bi^{2+} centers suppress the formation of F centers. Figure 7 shows the formation of Bi^+ centers in the case of KBr crystals. The conversion of Bi^{2+} to Bi^+ is also limited to about 30%, and there is a saturation effect. The Bi^+ centers can be formed in the other alkali halide crystals also, and the data obtained in the case of a number of alkali halides are given in Table IV.

In the case of KBr crystals containing bismuth in both its trivalent and divalent states, the effects are similar and a marked increase in the Bi^{2+} band is found, besides a small Bi^+ band. This is because of electron capture by the Bi^{2+} centers.

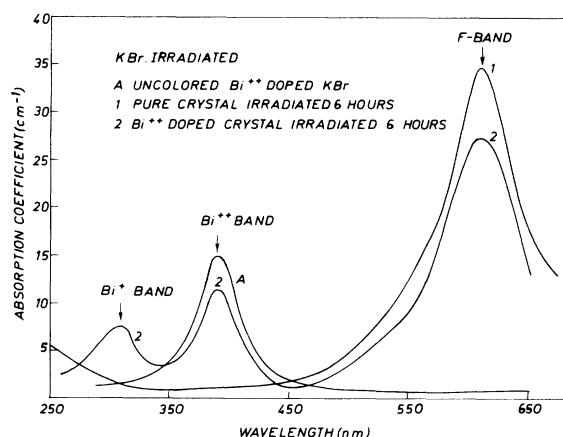


FIG. 7. Optical absorption of KBr crystals containing divalent and x-irradiated bismuth.

The fact that bismuth reduces in valence state after radiation damage makes it similar to impurities like Pb^{2+} , Cd^{2+} , etc., where reduced valence states have been reported.⁹

B. Additively colored crystals

1. Optical-absorption studies

Figure 8 shows the spectrum of an additively colored alkali halide crystal originally containing Bi^{3+} bands. It can be seen that besides the F band, another prominent band is observed in the uv-region at 310 nm in the case of a KBr crystal. This is the region where the Bi^+ band was found in irradiated KBr crystals. The band at 310 nm, observed in additively colored KBr crystals, is attributed to Bi^+ centers formed by the Bi^{3+} centers trapping the electrons available in the process of additive coloration. If the coloration is done in a crystal in which Bi^{2+} is dominantly present,

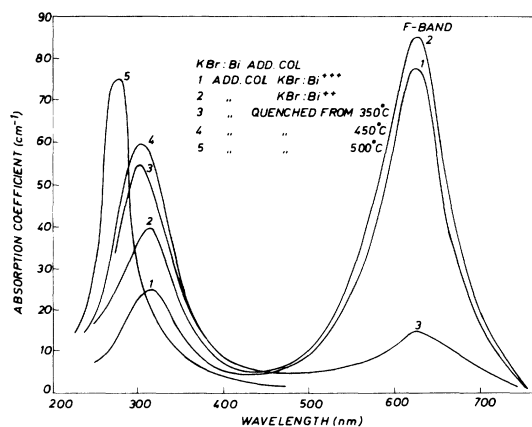


FIG. 8. Bi^+ , Bi^0 , and bismuth colloidal bands in additively colored and appropriately treated KBr crystals.

TABLE IV. Optical bands due to Bi⁺ and atomic and colloidal centers of bismuth in alkali-halide crystals.

Crystal	Lattice constant (Å)	Bi ⁺ bands ^a					
		Peak positions (nm)		Half-width (eV)		Bi ⁰ (nm) ^b	Bi-colloid (nm) ^b
		RT ^c	LNT ^d	RT	LNT		
NaCl	5.628	305	300	0.5	0.45	290	275
KCl	6.28	305	295	0.55	0.5	295	275
KBr	6.59	310	303	0.6	0.53	300	275
KI	7.052	310	305	0.5	0.45	305	280
RbCl	6.54	310	305	0.5	0.43	300	275

^aFormed by irradiation.^bFormed by additive coloration.^cRoom temperature.^dLiquid-nitrogen temperature.

the intensity of the Bi⁺ band is much greater, as seen from curve 2 in Fig. 8. Curves 3, 4, and 5 show the result of quenching these crystals rapidly after heating them at 350, 450, and 500 °C for 1 h at each temperature. It can be seen that on quenching the crystal from 350 °C, the *F* band has considerably reduced in intensity, and the Bi⁺ band has also been reduced in intensity while a new band starts rising at 300 nm. In view of the fact that the Bi⁺ centers are also reduced in intensity along with the *F* band, it is postulated that the electrons released from the *F* band are trapped by Bi⁺ centers to form Bi⁰ centers. Quenching from higher temperatures gives rise to a sharper and much more intense band at 275 nm. This band is attributed to the colloids of bismuth which are coagulates of atomic bismuth. At higher temperatures, the atomic bismuth becomes mobile and coagulates to form these colloidal centers. The intensity of this colloidal band is a function of temperature of quenching, time for which the sample is heated at a particular temperature (≥ 500 °C), and concentration of bismuth in either divalent or trivalent states. Furthermore, as is to be expected, the band is not temperature dependent, and the width also is not influenced by temperature. These features imply that the centers are weakly coupled to the lattice, and form a separate phase inside the crystal. Table IV also shows the peak position observed in the case of different alkali halides where atomic and colloidal bismuth are found and studied in the present work. Such colloidal centers and associated optical-absorption bands have been observed in the case of other metal impurities.⁹⁻¹¹

2. Electrical conductivity studies

The essential interest in the studies of electrical conductivity in colored crystals is to see if they exhibit any special features which are acquired by the process of coloration. Optical results have shown that if bismuth-doped alkali

halides are additively colored and quenched from progressively higher temperatures, atomic and colloidal bismuth centers are formed. Figure 9 shows a plot of σ_c/σ_n vs temperature (σ_c is conductivity of colored crystals and σ_n is conductivity of the normal uncolored but impurity-doped crystal) in the case of KBr crystals containing 80 ppm bismuth. Such a plot shows that as the temperature is raised two regions of large conductivity in temperature regions ~ 200 and ~ 600 °C are observed. The cause for this abnormal rise must be sought in the behavior of colored crystals. The increase of conductivity in the region ~ 200 °C has been observed earlier, and has been attributed to thermal ionization of *F* centers.^{9,10} However, the second increase beyond 500 °C is now attributed to thermionic emission from bismuth colloids which are formed prominently in crystals quenched from 500 °C. As the crystals are quenched from higher temperatures, more colloids break, and an enhanced conductivity is found. There is no peak observed in such a conductivity. First, measurements have not been

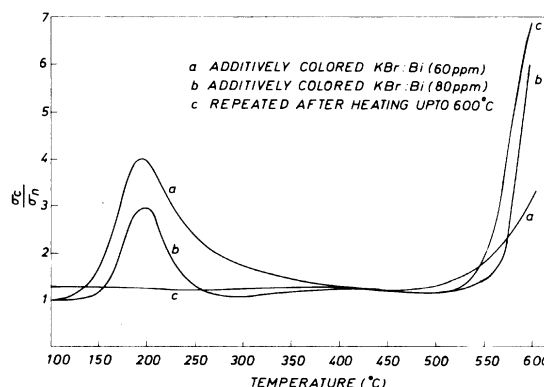


FIG. 9. Plot of σ_c/σ_n vs temperature. σ_c is the conductivity of colored crystals and σ_n is the conductivity of the normal uncolored but impurity-doped crystal).

possible beyond 600°C, and second, bismuth has a work function of 4.5 eV, which means that even at 600°C some colloids remain. This interpretation is based on a similar interpretation given for such enhanced conductivity observed in pure KCl crystals.¹⁰ Curve C of Fig. 9 shows σ_c/σ_n vs temperature for crystals which are colored and quenched from 600°C. Although several colloids break up, the process of formation continues until atomic bismuth centers are present.

3. ESR absorption

The results of ESR measurements on crystals in which bismuth colloids have been formed as described in previous sections are discussed here. Additively colored crystals give the characteristic *F*-center ESR signal which dies down as the crystals are quenched from successively higher temperatures (>250°C). As the crystals are quenched from progressively higher temperatures, no ESR signals are observed. If, however, the quenching is done from 500°C, a new ESR line appears. This line has a width of 18 G and is isotropic. The *g* value measured from the observed spectrum is 1.998. The line shape is analyzed to be Lorentzian. Like the optical band, the ESR signal is temperature insensitive, and its intensity is a function of quenching temperature, time of heating at a particular temperature, and concentration of bismuth. This ESR signal is attributed to conduction electrons of the bismuth colloids. The particular features of the signal which allow its assignment to the conduction electrons are (a) its correlation with optical band and enhanced conductivity, (b) its near-free-spin *g* value, (c) its Lorentzian line shape, and (d) its temperature independence of width. Such ESR signals attributed to colloids of metal particles in alkali halides have been reported in the case of lithium,¹² potassium,¹⁰ and cadmium,⁹ and the parameters are shown in Table V. This evidence, obtained from ESR studies, is in strong support of results of optical absorption and conductivity.

TABLE V. The half-widths, line shape, and *g* values for conduction-electron spin resonance, absorption in alkali halides containing metallic colloids.

Crystal	Metal colloids	Half-width (G)	<i>g</i> factor	Line shape	Reference
KCl	K	2.5	1.998	Lorentzian	10
	Cd	150	1.999	Lorentzian	9
	Bi	25	1.993	Lorentzian	present work
KBr	K	6	1.9997	Lorentzian	10
	Cd	150	1.98	Lorentzian	9
	Bi	18	1.998	Lorentzian	present work
NaCl	Bi	15	1.998	Lorentzian	present work
LiF	Li	10	2.0023	Lorentzian	12

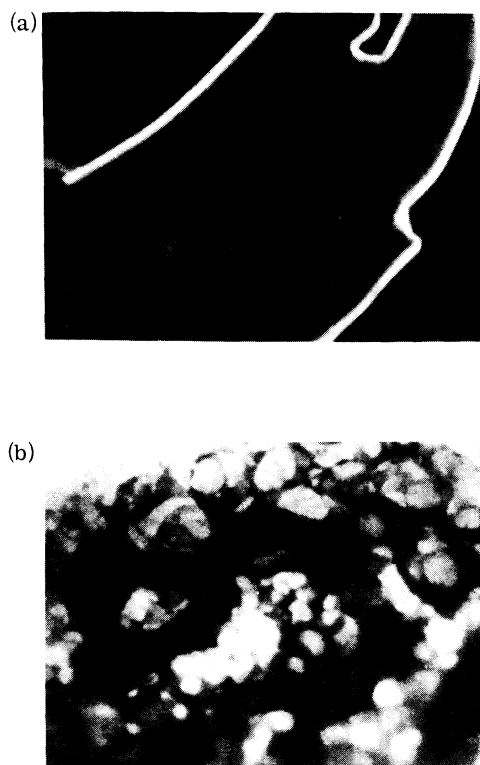


FIG. 10. (a) Electron micrograph of a pure KCl crystal (white border refers to the edge of the crystal, magnification 28 000×). (b) Electron micrograph of Bi colloids in KCl:Bi crystal (magnification 28 000×).

4. Electron microscope observations

It has been shown in the previous section that additively colored and quenched bismuth-doped alkali halides show a prominent band at 275 nm, give enhanced conductivity in the temperature region ~500°C, and give characteristic ESR spectra, and these features have been attributed to formation of colloids of bismuth under suitable conditions. It was then thought desirable to study structural features of such crystals and note the differences between such crystals and crystals which do not contain colloidal particles. Figure 10(a) shows an electron microscopic photograph of a pure alkali-halide crystal with a magnification of 28 000×. Under identical conditions crystals containing colloids have also been studied, and Fig. 10(b) shows the presence of colloids clearly. The observations were made at liquid-nitrogen temperature to reduce the thermal agitation in the sample. From such studies an approximate idea of the size of the colloids has been obtained as 40 atoms per colloid as an average. However, there are colloids with varying sizes. The size of the colloids seem to be determined by the tem-

perature of quenching and the time for which they are heated at a particular temperature. As can be seen, the colloids are not uniformly distributed in the crystal, but appear to be concentrated at particular sites. This evidence did not come from any of the other techniques used. The fact that the colloids are found at certain specific

points in the crystal is to be explained by the fact that when Bi^0 centers are made mobile, they tend to coagulate or cluster around nucleation centers which are scattered at certain positions. Although there is no specific evidence in this work, it appears that dislocations act as such nucleation centers.

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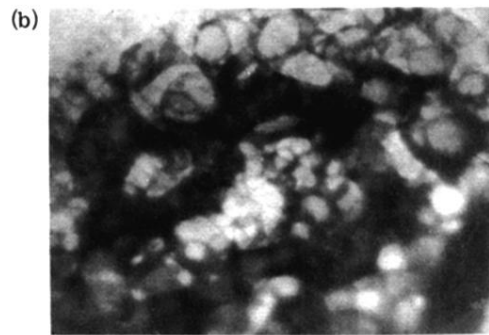
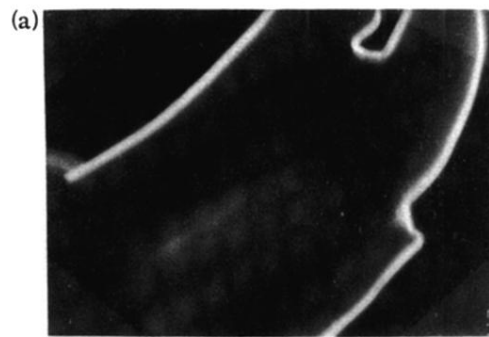


FIG. 10. (a) Electron micrograph of a pure KCl crystal (white border refers to the edge of the crystal, magnification 28 000 \times). (b) Electron micrograph of Bi colloids in KCl:Bi crystal (magnification 28 000 \times).