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On the analogy between local modes and color center absorption bands

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Résumé. — Les bandes d’absorption et d’émission des centres colorés sont comparées aux modes localisés de vibration dus aux ions H⁻ et D⁻ qui se substituent aux ions d’halogène dans les halogénures alcalins. On trouve que l’énergie des maxima de ces bandes est proportionnelle à l’énergie des modes localisés des ions H⁻ et D⁻. En raison des corrélations présentées, les bandes des centres colorés sont considérées comme des modes localisés vibrationnels. Bien que ce modèle soit trop simple, on peut en tirer une série de prédictions qui sont en bon accord avec les résultats expérimentaux.

Abstract. — The absorption and emission bands of F aggregate centers are compared with the local modes of H⁻ and D⁻ ions substituting the halogen ions in alkali halides. It is shown that the energies of the band maxima of F aggregate centers are proportional to the local vibrational mode energies of the H⁻ or D⁻ ions. Because of these correlations, the bands of the F aggregate centers are considered to be due to the excitation of local harmonic oscillators. From this simple picture — how oversimplified it may be — a series of predictions can be drawn, which are in fair agreement with experiment.

1. Introduction. — U centers in alkali halides are due to H⁻ or D⁻ ions which substitute the heavier halogen ions. The appertaining local modes are the U infrared absorption bands which have been detected by Schäfer [1] in several alkali halides.

Since the H⁻ and D⁻ ions are much lighter than the surrounding ions, the local modes can be considered as oscillations of these ions in a spherical harmonic oscillator potential well set up by the static lattice. The excitation energy of these local oscillators is given by

\[ E = \hbar \omega = \hbar \sqrt{K/m} \]

with the force constant \( K \) and the mass \( m \) of the impurity. In the same manner, Rosenstock and Klick [2] considered also the F band in alkali halides as a local mode due to the electrons which replace the anions.

Assuming that \( K \) is independent of the impurity mass \( m \), the energies of the F absorption bands \( E_F \) are expected to be proportional to the energies \( E_u \) of the U bands with

\[ E_F/E_u = \sqrt{m_{\text{H}^-}/m_e} = 43 \]

Since \( K \) is nearly independent of the impurity mass \( m \), the energies of the F absorption bands \( E_F \) are expected to be proportional to the energies \( E_u \) of the U bands with

\[ E_F/E_u = \sqrt{m_{\text{H}^-}/m_e} = 43 \]

From figure 2 one can take \( E_F/E_u = 40 \) which differs only slightly from the expected value.

Figure 2 shows that besides \( E_F \) also the energies of the F luminescence bands are proportional to \( E_u \). The emission energies, however, are smaller than the absorption energies by a factor of about 2 because the excited state of the F center relaxes before emission, i.e. during the lifetime of the excited state the lattice surrounding the F center cannot be considered to be static (Franck-Condon principle).

Because of the close relationship between the local modes and the F center absorption bands, we tried — like in figures 1 and 2 — to extend by analogy the simple picture of local oscillators to F aggregate centers. The chief aim of the present paper is to search how well and how far this oversimplified model yields a crowd of predictions and relations between the different color center absorption bands, most of which turn out to be in
fair agreement with experimental results. In the following this will be shown in detail. For all figures of the present paper, we used experimental data reported in the literature for temperatures below 100 K. In this temperature range the half-widths of the bands are relatively small and the band maxima do not shift with the temperature appreciably.

2. F aggregate centers. — Bleaching the F band one can readily convert F centers into F aggregate centers. The position of the corresponding absorption bands as well as the structure of many F aggregate centers are well known [3, 4].

On the other hand, the aggregation of U centers needs rather refined techniques [5]. Therefore the \((\text{H}^-)_2\) and \((\text{D}^-)_2\) centers, only, which are formed by two neighbouring U centers, have been investigated in KCl, KBr, KI, NaCl, and RbCl [6]. Obviously, one can consider these centers to be built from two single local oscillators. In fact, M. de Souza and F. Lüty [7] applied the model of two coupled local oscillators to these centers successfully. After fitting the force constants with respect to the static lattice as well as the coupling force constant of the oscillators, they calculated the energies of the pair modes. The in-phase modes of these coupled oscillators can be compared with the absorption bands of the M or F2 centers, which consist of two neighbouring F centers each. (To simplify arguments we suppose the M or F2 centers as well as the \((\text{H}^-)_2\) and \((\text{D}^-)_2\) centers to be orientated in the [110] direction.)

At first we tested whether the corresponding \(\text{F}_2\), \(\text{H}_2\) and \(\text{D}_2\) center absorption band maxima \(E\) fit the relation \(E \sim m^{-0.5}\) according to equation (1). With the experimental data available from the literature [3, 5-7] we found always \(E \sim m^{-n}\) with \(n\) close to 0.5. For the longitudinal in-phase modes (transition moment parallel to the [110] direction) in KCl this is shown in detail by the open circles in figure 1a (upper scale) : The dashed line represents \(E \sim m^{-0.44}\). From the figure one can see that these values are shifted to lower energies as compared to the \(\text{H}^-\) or \(\text{D}^-\) local mode or F band maxima. On the other hand, the excitation energies for the transversal (with respect to the [110] direction) in-phase modes
are known to coincide nearly with those of the single oscillators, i.e. the H\textsuperscript{−}, D\textsuperscript{−} or F centers [3, 5-7]. These experimental facts are in good agreement with our expectation that the coupling of neighbouring F or U centers is effective in the [110] direction, only, whereas the coupling to the surrounding lattice remains nearly unchanged. Then, the longitudinal in-phase mode (called M\textsubscript{1} band) of the M or F\textsubscript{2} centers should be reduced by the factor

\[ \sqrt{m/(2m)} = 1/\sqrt{2} \]

with respect to the energy \( E_F \) of the F band. In fact the energies \( E_M \) of the M\textsubscript{1} band maxima are shifted to lower energies on an average by the factor 0.63 which differs slightly from the expected value

\[ 1/\sqrt{2} = 0.707 \].

Taking into account the mass 2 \( m_e \) of the M center, one can estimate the M\textsubscript{1} absorption band maximum even from \( E_u \). Figure 3 shows in detail the proportionality between the energy \( E_u \) of the U infrared band and the energies of both the M\textsubscript{1} absorption and M emission (dashed line) band maxima. The full curve corresponds to the ratio \( E_M/E_u = 25 \) which differs by 20 % from the value \( \sqrt{m_{M}/(2m_e)} \approx 30 \) expected if the coupling of the M centers and that of the U centers to the surrounding are exactly the same.

![Figure 3: M\textsubscript{1} absorption (○) and M emission (●) band energies \( E \) versus the U infrared absorption band energy \( E_u \). (Data from Refs. [1, 16, 17, 20-24].)](image)

U aggregate centers built with more than two U centers have not been investigated until now. Therefore, one cannot compare other F and U aggregate centers directly. Since the force constants do not vary appreciably with the impurity mass, however, one expects the absorption and emission bands of the other F aggregate centers to be proportional to the U infrared absorption band, too.

In order to prove this idea, we plotted the energies of the absorption and — as far as they are known — emission bands of F aggregate centers in different alkali halides as a function of the corresponding U infrared absorption band energy. Indeed, the F\textsuperscript{2}\textsuperscript{+} absorption and emission bands and the M\textsuperscript{′} absorption band are approximately proportional to the U infrared absorption band (Fig. 4) as well as the R\textsubscript{1}, R\textsubscript{2} absorption and the R emission bands (Fig. 5). The same proportionality is shown in figure 6 for the F\textsuperscript{−}, R\textsubscript{1}, R\textsubscript{2} absorption bands and the F\textsuperscript{−} emission band. Figure 7, finally, shows that also the N\textsubscript{1} and N\textsubscript{2}

![Figure 4: The F\textsuperscript{2}\textsuperscript{+} absorption (○) and emission (●) and the M\textsuperscript{′} absorption (○) band energies \( E \) (●: M\textsuperscript{′} zero-phonon line) versus the U infrared absorption band energy \( E_u \). (Data from Refs. [1, 16, 21, 24-34].)](image)

![Figure 5: The R\textsubscript{1} (○) and R\textsubscript{2} (●) absorption and the R emission (+) band energies \( E \) (●: R\textsubscript{2} zero-phonon line) in dependence of the U infrared absorption band energy \( E_u \). (Data from Refs. [1, 16, 20, 22, 23, 27, 29, 30, 32, 35-37].)](image)
Fig. 6. — The F′ absorption (○) and emission (●) and the R′₁ (○) and R′₂ (+) absorption band energies \( E \) (● R′ zero-phonon line) versus the U infrared absorption band energy \( E_u \). (Data from Refs. [1, 16, 22, 26-28, 31, 32, 34, 38, 39].)

Fig. 7. — The N₁ (○) and N₂ (●) absorption band energies \( E \) as a function of the U infrared absorption band energy \( E_u \). (Data from Refs. [1, 16, 22, 23, 29, 32, 33, 40, 41].)

Absorption bands are proportional to \( E_u \). The zero-phonon lines of the M′, R₁ and R′ bands, too, fit very well the same relations as can be seen in figures 4, 5 and 6.

In addition, we tried to correlate also the F′ band to the U infrared band. In this case, however, the correlation is very poor. The reason may be that the F′ band corresponds to transitions directly into the non-localized states of the conduction band [3].

3. Discussion. — In the preceding section we showed that the color center absorption bands (and even some emission bands) are proportional to the excitation energies of the local modes of U centers in alkali halides. These empirical correlations can be understood on the basis of a harmonic oscillator model, since the masses of the corresponding defects are much lighter than the ion masses of the surrounding lattice.

In spite of the crudeness of this simple picture there is a series of prediction, which have been shown in the preceding section to be in fair agreement with experiments.

On the other hand, besides the local oscillator model there exists another elementary model of the F center. The model of an electron in a three-dimensional potential box with infinite walls [8-10]. In this case the energy needed to excite the electron from the ground state is related to the length \( a_0 \) of the potential box by

\[
E = \frac{3\hbar^2}{8ma_0^2}.
\]

If one assumes the length \( a_0 \) to be about 2 times the nearest neighbour distance, one expects the energy of the F-band

\[
E_F \sim a_0^{-n}
\]

with \( n = 2 \) which is known as the Mollwo-Ivey relation [8, 9]. In fact, there is a remarkably good agreement with experiments, since the experimental values of the F band maxima can be fitted by the relations \( E_F \sim a_0^{-1.81} \) for the alkali halides with NaCl-structure and \( E_F \sim a_0^{-2.28} \) for those with CsCl-structure [11]. Unfortunately one needs two relations, even if equivalent interionic distances are used.

In order to understand why the F band maxima are related both to \( a_0 \) and to the U infrared band, we point out that both relations (1) and (2) are due to different approximations of the average potential for the electron bound to the halogen-ion vacancy: The approximation by the particle-in-a-box model is based on the assumption that the lattice constant should obviously be an appropriate scaling parameter for the defect potential. On the other hand, in the local oscillator model this potential is approximated by a harmonic potential which should be nearly the same for the H⁻ ion and the electron. Since in figure 2 the F band energies are related directly to the U band energies, the scaling of these energies with respect to the nearest neighbour distance \( a_0 \) does not appear explicitly. In this way, one takes into account that the ions around the defects are shifted from their usual lattice sites. This turns out to be very useful for the application of the oscillator model to the bands of aggregate centers, as is shown in the preceding section.

On the other hand, there are great difficulties to extend the particle-in-a-box model to other color centers and other defects, where the exponent \( n \) in relation (3) deviates considerably from 2. For instance, the M₁ bands of the F₂ or M centers in the alkali halides are fitted by the relation \( E_{M_1} \sim a_0^{-1.56} \) [9]. There is no simple physical model to account for this scaling law.
Furthermore, in the particle-in-a-box model the $M_1$ band is expected to be shifted to lower energies with respect to the $F$ band by a factor of about $1/4$, because the length of the potential box has been doubled approximately. Instead, one observes experimentally a factor of about 0.625 \(^{(1)}\). This factor is close to $1/\sqrt{2}$ which is expected for the longitudinal in-phase mode of two coupled oscillators.

Similar considerations can be made for the absorption band of the other $F$ aggregate centers. According to the particle-in-a-box model one expects that most of the absorption bands are shifted to lower energies by much larger amounts than those observed in experiments. However, we must admit that we cannot give from our crude oscillator model a priori predictions for the ratios of other bands to the $F$ band such as $E_{M_1}/E_F$, $E_{N_1}/E_F$, etc. which are as good as that for the ratio $E_{M_1}/E_F$. The reason may be that the coupling of the electrons to the surrounding lattice changes because of the aggregation.

Nevertheless, the obvious relations shown in the figures can help to identify new absorption bands. To give an example of the predictive power of the present model we consider the absorption bands of color centers in LiH: According to the Mollwo-Ivey relations one expects that the color center absorption bands in LiH coincide approximately with those of LiF, since the nearest neighbour distances of the ions in both materials are nearly the same (LiH : 2.04 Å; LiF : 2.01 Å). Thus the $F$ band maximum, for instance, should be observed at 4.8 eV. Therefore the position of the $F$ band maximum in LiH, which has been observed experimentally at 2.4 eV \([12]\), has been questioned \([13]\). If one applies the simple oscillator model, however, one can identify the energy of the $U$ infrared mode with the TO phonon energy of 0.073 eV \([14]\). Then, according to the relation indicated by the full line in figure 2, one expects an energy of about 2.9 eV for the position of the $F$ band maximum in LiH. This value is in much better agreement with the experimental result of 2.4 eV than the value of 4.8 eV predicted by the Mollwo-Ivey relation. Furthermore, the Mollwo-Ivey relations predict for the $M_1$ and $N$ band maxima in LiH the values 2.7 eV and 2.3 eV, whereas experimentally the maxima are observed at 1.7 eV and 1.3 eV. Thus there is a large discrepancy, too, between the expected and the observed values of the absorption band maxima which belong to $F$ aggregate centers. On the other hand, from the relations shown in figures 3 and 7 the corresponding maxima should be observed at about 1.8 eV and 1.4 eV. These data are in fair agreement with the experimental values.

In \([12]\) the $R$ band maxima have been tentatively assigned to indications of weak absorption bands in the 1.4 to 1.6 eV range. According to the relation in figure 6, however, one expects in that energy range for LiH rather the $F_2^+$ band than the $R$ bands. On the other hand the $R$ band maxima are expected at about 2.3 eV and 2.0 eV according to figure 5. In fact, Pretzel and Rushing observed near these energies several bands, which they did not associate definitely to specific centers. For instance, the $A$ band at 2.1 eV (see Fig. 5 in \([12]\)) seems to be a superposition of two bands because of its asymmetrical shape. These bands may correspond to the $R_1$ and $R_2$ bands. Since, however, both absorption bands are not resolved sufficiently in the figures of \([12]\), this tentative assignment is worth-while reexamining experimentally.

We believe that the relations between color center absorption bands and the $U$ infrared bands, which have been discussed in the present paper, can serve to associate unidentified absorption bands to certain centers not only in the case of LiH but also in other cases. Many further examples may be given by the absorption bands of the higher $F$ aggregate centers with and without additional charge, which are not yet known for quite a large number of alkali halides.

4. Conclusion. — The energies $E_F$ of the $F$ absorption band maxima are proportional to the local vibrational mode energies $E_a$ of the $U$ centers \([2]\).

The experimental ratio $E_F/E_a\approx 40$ is close to 43. This value is expected if — in analogy to the $U$ infrared band of the $H^-$ ions — the $F$ band is considered to be due to the excitation of local vibrations of an electron bound to a halogen vacancy. This model of local harmonic or several coupled harmonic oscillators has been extended successfully to the $F$ aggregate centers using experimental data available from the literature. In all cases there is a rather fair — to some extend even quantitative — correlation to the local modes of the $U$ centers.

The observed relations can help to identify absorption bands of other color centers. This has been demonstrated in some detail for the color center absorption bands in LiH.

One often observes that the color center absorption bands are also related to the nearest neighbour distance or the lattice constant in the alkali halides, which are known as Mollwo-Ivey relations. These correlations, however, are not reliable in their predictive power, as has been shown in some cases. Furthermore the Mollwo-Ivey relations can be established \textit{a posteriori} only, since the exponent for the lattice constant may differ considerably from the expected value — 2.

\(^{(1)}\) With $E_F/E_a = 40$ from figure 2 and $E_{M_1}/E_a = 25$ from figure 3 one derives $E_{M_1}/E_F = 0.625$. Contrary to this, one obtains $E_{M_1}/E_F = \text{constant} \times a_0^{-0.25}$ with $E_F \approx a_0^{-1.81}$ and $E_{M_1} \approx a_0^{-1.58}$ from the Mollwo-Ivey relations.

In order to examine this discrepancy, we plotted the ratio $E_{M_1}/E_F$ of the experimental data from figures 2 and 3 as a function of $a_0$. According to this plot, $E_{M_1}/E_F = 0.625$ seems to fit the experimental data better than relation $E_{M_1}/E_F \approx a_0^{-0.25}$. However, one cannot decide definitely what relation is better, because the experimental data scatter too much. Furthermore, the useful range of $a_0$ is rather small, since $a_0$ varies by a factor of 1.96 between CsI and LiF corresponding to a variation of $a_0^{-0.25}$ by a factor of 1.18 only.
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