

The $3d \rightarrow 4p$ transitions of Cu^+ in LiCl and of transition-metal ions in crystals*

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An intense absorption band due to Cu^+ in alkali halides has been observed. In $\text{LiCl}:\text{Cu}^+$ it occurs at 57300 cm^{-1} . Its three-dimensional oscillator strength is $f = 0.070$. It is shown that this band is primarily a $d^{10} \rightarrow d^9p$ transition. The $d \rightarrow p$ transition energy in the crystal is substantially lower than in the free ion, although the $d \rightarrow s$ transition energy is higher. The near-uv bands are discussed in the light of this new observation. We believe that the present assignment opens the way for $3d \rightarrow 4p$ band assignments in other ions in crystals, and several have been suggested.

Electronic transitions occurring in ions in crystals can often be assigned to localized atomlike transitions. Well-known examples are the $d-d$ transitions of transition-metal ions and $s^2 \rightarrow sp$ transitions in the Tl^+ -like ions.¹⁻³ In this paper, we will make the assignment of a $3d^{10} \rightarrow 3d^94p$ transition in Cu^+ in a LiCl host crystal. Although $d-p$ transitions have been proposed before for various cases of ions in crystals, we believe the present example is the clearest case. From this example, support can be drawn for several other $d-p$ assignments.

These assignments are important for several reasons. They extend the range of the known localized excitations of ions in crystals and make us wonder if still higher localized transitions are possible. The assignments also make it possible to insert definite values of the $d-p$ energies in calculations of transition probabilities and other electronic properties dependent on p -orbital energies.

The particular advantage of the host crystal LiCl used in these experiments is that it is transparent to 1550 \AA , and thus, it appears to be the most transparent chloride known. It is relatively easy to incorporate Cu^+ in this host, while it is difficult to get it into the more transparent fluoride host crystals such as LiF.

EXPERIMENTAL

The doped crystals studied were all grown in this laboratory by a modified Bridgeman technique. Great care was taken in the preparation of all samples used in these experiments to avoid incorporation of any but the intended impurities in the LiCl host crystals. Since LiCl is a very hygroscopic and deliquescent material all handling was carried out in either dry nitrogen or high vacuum ambients. If crystals are properly treated they will exhibit good optical transparency out to the first exciton band edge of the pure salt at about 8.4 eV .⁴ No absorption bands can be observed at lower ener-

gies in pure LiCl crystals which have been prepared with our methods.

The starting material for crystal preparation was E and M Chemicals' suprapure LiCl, which was dried in a quartz vacuum oven prior to use. The Cu^+ ion was introduced directly into the melt by reacting 99.999%-purity Cu metal, obtained from Gallard Schlessinger Co. with Matheson electronic grade HCl at high temperature. In order to insure reproducibility of results, several samples were grown and studied.

The near-uv spectrum was recorded on a Cary 14R spectrophotometer. The far-uv region was covered by a McPherson 2-m vacuum grating monochromator. A Xe microwave discharge lamp was used as a source of vacuum-uv radiation. A computer interfaced photon counting system was used to analyze signals from an EMR phototube with a CsTe photocathode.⁵ Finally, variable temperature measurements were made possible by an Air Products Helitran unit.

RESULTS

The spectrum of the $\text{LiCl}:\text{Cu}^+$ system is shown in Fig. 1 at both 10°K and room temperature. It consists of three absorption bands in the near uv. The highest energy band (III) is only observable at low temperatures. A band system with a very similar appearance can also be observed in the $\text{NaCl}:\text{Cu}^+$ doped system.² More recently, band I has been attributed to the absorption of Cu^+ ion pairs.⁶ Reference 6 also shows qualitative agreement with our observations with respect to the temperature dependence of these bands. Band I shows a relatively small increase of oscillator strength with temperature and no change in peak position. Band III appears to show no dependence on sample temperature at least below 70°K where it is strong enough to be observed. In contrast to this, band II shows a shift in peak position of 650 cm^{-1} to higher energy and a decrease

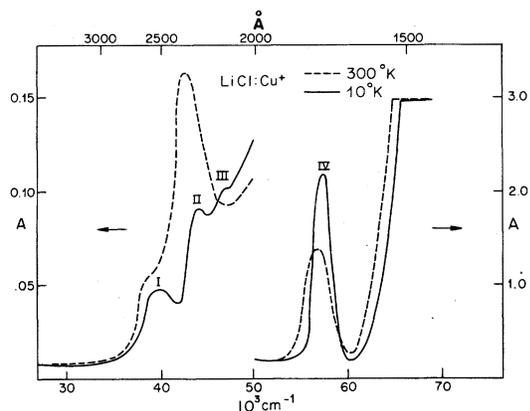


FIG. 1. Absorption spectrum of LiCl:Cu⁺ sample at 300 and 10°K. The optical density, *A*, (O.D.) of the near-uv spectrum was reduced by a factor of 0.173 to correspond to concentration and path length of the vacuum-uv sample. The relation between optical density and molar extinction coefficient in this figure is $\epsilon = 3440A$.

in oscillator strength of about 4 times on cooling from room temperature to 10°K.

In the vacuum region of the spectrum, a very intense absorption band is present at 57 000 cm⁻¹. It has a measured oscillator strength which is about two orders of magnitude greater than those of bands I, II, and III. Upon cooling from room temperature to 10°K no significant change in oscillator strength can be noted, although some change in band shape can be seen. The energy of the band peak is, however, blue-shifted by 550 cm⁻¹ upon cooling. The pertinent parameters of the spectra are listed in Table I. Because of the large difference of band intensity between the near- and far-uv band systems, two different sample concentrations of Cu⁺ had to be used.

TABLE I. Band positions and oscillator strengths for the absorption bands observed in the LiCl:Cu⁺ crystal samples. Oscillator strength is based on the analytical concentration of the samples; however, bands I and III are probably due to Cu⁺ pairs of unknown concentration, and have higher oscillator strength than shown.

Band	Temp. (°K)	Energy (cm ⁻¹)	<i>f</i>
I	10	39 370	1.5×10^{-3}
	300	39 370	2.1×10^{-3}
II	10	43 670	2.3×10^{-3}
	300	43 010	9.1×10^{-3}
III	10	47 170	3.6×10^{-3}
	300	56 750	0.067

DISCUSSION

In agreement with previous workers,⁷⁻⁹ we assign the absorption band II at 43 000 cm⁻¹ to the ${}^1A_{1g}(3d^{10}) \rightarrow {}^1E(3d^94s)$ transition. This assignment appears secure because of the band's observed strong temperature dependence and its relatively low oscillator strength. Since $d \rightarrow s$ is parity forbidden, it is not surprising that the transition probability is induced by vibrations, which account for the temperature dependence of band II. A plot of $\coth^{-1}[I(T)/I(0)]$ vs $1/T$ gives a good straight line from whose slope the frequency of the enabling vibration is found to be 99 cm⁻¹, Fig. 2. [Here $I(T)$ is the band area and T the absolute temperature.]

It is important to note that there is no deviation from linearity in Fig. 2. This result indicates that in LiCl, Cu⁺ is precisely at a Li⁺ site, and does not lie off-center as it does when in some other alkali halides.^{10,11} The reason for the on-center position in this case is probably because of the very small radius of Li⁺, 0.7 Å, whereas the standard ionic radius of Cu⁺ is 0.96 Å.

The small size of the substitutional site is manifested in the spectrum in another way. It is known that the $3d^{10} \rightarrow 3d^94s$ band energy is almost independent of the host crystal, occurring at 40 000 cm⁻¹ ± 1 000 cm⁻¹ in most other alkali-halide host crystals. In LiCl, however, this band occurs nearly 3500 cm⁻¹ to higher energy. We believe that this "blue shift" is due to the small size of the site, causing a strongly antibonding interaction of the Cl⁻ 4*p* orbitals with the Cu⁺ 4*s* orbital. This antibonding interaction is also evidenced by the temperature shift given in Table I, and is now well established for other $d \rightarrow s$ transitions.^{5,10,12}

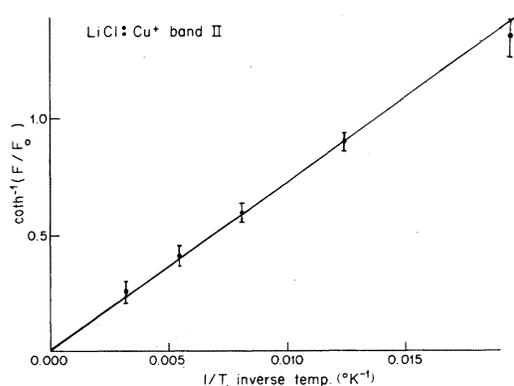


FIG. 2. Hyperbolic cotangent plot of the oscillator strengths for band II as a function of temperature. F_0 is the oscillator strength at the lowest temperature measured. The oscillator frequency obtained from this plot is 100 cm⁻¹.

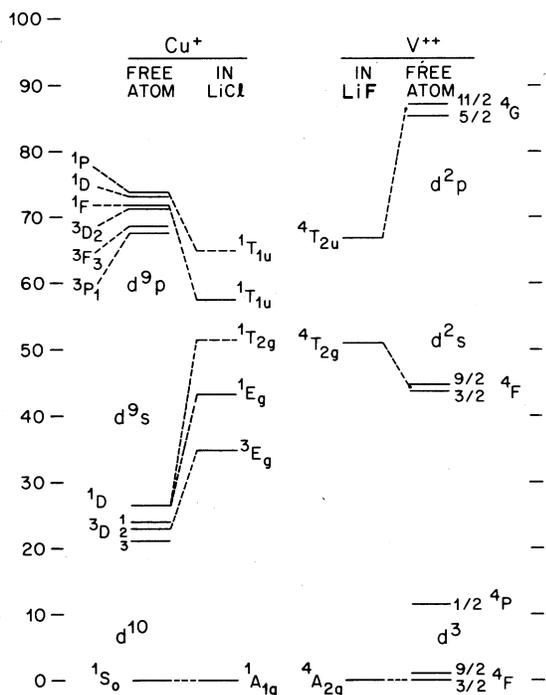


FIG. 3. Energy-level diagram for Cu^+ and V^{++} in free state and in a crystal host. Some components of multiplet states have not been shown. Band maxima are used for crystal energy levels except for 3E of Cu^+ where the zero-phonon line position was estimated.

The shift of band IV to higher energies as the temperature is lowered indicates that this band is also due to a transition localized on the Cu^+ . Unlike the $3d \rightarrow 4s$ band (II) its intensity does not change significantly when the temperature is lowered (Table I), and it is therefore an allowed transition. The assignment $3d \rightarrow 4p$ for this band is thus reasonable, but we must also consider the possible charge transfer transitions.

In another publication we will show the behavior of the charge transfer transitions of divalent transition-metal ions in LiCl . For example, it is found that Mn^{++} has a chloride-metal band at $57\,800\text{ cm}^{-1}$ with $f=0.03$ at room temperature, and upon cooling to 10°K , it shifts to $58\,000\text{ cm}^{-1}$, with no change of oscillator strength. The energy shift on cooling in this case is less than one third of the value found for band IV of Cu^+ in LiCl , or for the $3d \rightarrow 4s$ transition, band II, or for the $3d \rightarrow 4s$ transition in fluoride host crystals.¹²

Another argument against the charge transfer assignment for band IV of Cu^+ is that there are no empty d orbitals, and the chloride electron would have to be promoted to the next excited $4s$ orbital. This would make its energy much too high to be assigned reasonably to band IV.

There is one difficult point in making the $3d \rightarrow 4p$ assignment which we must now discuss. In the case of the $3d \rightarrow 4s$ transitions of transition-metal ions in fluoride host crystals, the observed bands occur within 0.5 eV of the corresponding transitions in the free ions. For Cu^+ in LiCl , the $3d \rightarrow 4s$ band is raised 2.7 eV above its free-ion value, showing that there is strong repulsive interaction between the chlorides and the Cu^+ $4s$ electron. Band IV, however, is nearly 2 eV below the $3d \rightarrow 4p$ transition of the free ion. These shifts are illustrated in Fig. 3. If band IV is to be assigned as a localized transition, we must explain why its relation to the free-ion energy differs so sharply from that of the localized $3d \rightarrow 4s$ band.

A $4p$ orbital is more strongly directed than $4s$ and can therefore be expected to utilize any unfilled Cl^- orbitals more effectively for bonding than does $4s$. The $4s$ orbitals of Cl^- can form directed molecular-orbital combinations which provide some bonding between Cu^+ $4p$ and Cl^- $4s$, thus lowering the $4p$ energy. Furthermore, the $4s$ orbital of Cu^+ has a filled bonding partner to which it must remain orthogonal, while $4p$ does not. This increases the antibonding influence of the ligands for the $4s$ electron relative to that acting on the $4p$ electron.

These factors were included in molecular-orbital calculations in Cu^+ in alkali halides done by Yip and Fowler.¹³ Their results are in semiquantitative agreement with the present experimental observations if we make the $3d \rightarrow 4s$ and $3d \rightarrow 4p$ assignments to bands II and IV, respectively. The calculated shift of the $4p$ level to lower energies in the solid is only about a half of the value observed by us, although their calculations applies to NaCl , not LiCl . The calculated change in the $3d \rightarrow 4s$ energy is in the right direction also, but is somewhat too small. These calculations were done without any prior knowledge of the position of the $4p$ level. It would be interesting to repeat such calculations in order to get a better description of the $4p$ level. It must be strongly mixed with Cl^- orbitals; however, the high oscillator strength of band IV shows that there is a large component of Cu^+ $4p$ in its upper level.

Other experimental evidence has also been observed which may indicate the occurrence of $d \rightarrow p$ transitions. The first is the study¹⁴ of $\text{NaCl}:\text{Cu}^+$ which shows a rather strong absorption at $55\,500\text{ cm}^{-1}$. This band appears as a shoulder on the absorption band edge of the host. Second, a study in the far uv of the $\text{NaCl}:\text{Ag}^+$ and $\text{KCl}:\text{Ag}^+$ systems was done.¹⁵ This work revealed two bands in $\text{NaCl}:\text{Ag}^+$ at $55\,500\text{ cm}^{-1}$ and $61\,300\text{ cm}^{-1}$ with oscillator strengths of ~ 0.6 . In $\text{KCl}:\text{Ag}^+$, a single band is observed before the fundamental absorp-

tion at $57\,300\text{ cm}^{-1}$. In the KCl:Ag⁺ case, the $57\,300\text{ cm}^{-1}$ band was observed to shift to the blue by 400 cm^{-1} on cooling the crystal from room temperature to 80°K . This familiar characteristic of a localized transition supports the $d-p$ assignment for this band, and supports our assignment for the corresponding band of LiCl:Cu⁺.

Accepting the $3d-4p$ designation, let us consider the spectroscopic transition in more detail. The highest energy filled d orbital is of the E_g type. Thus the excited configuration of lowest energy must be $t_{2g}^6 e_g^3 p$, giving rise to the states ${}^1,3(T_{1u}, T_{2u})$. The states corresponding to the higher configuration $t_{2g}^5 e_g^4 p$ are ${}^1,3(A_{2u}, E_u, T_{1u}, T_{2u})$. In the free Cu⁺ ion, the 1P , 1D , and 1F states of d^9p lie within 2000 cm^{-1} of each other, and are above the triplets 3P , 3D , 3F by about 3000 cm^{-1} as shown in Fig. 3.¹⁶ Thus the $p-d$ electrostatic repulsion integrals are all small and crystal-field effects are expected to dominate the energy-level scheme. The only transitions allowed from the ground state $t^6 e^4 A_{1g}$ are to the two ${}^1T_{1u}$ states, and we believe that the upper state of the observed band IV must be predominantly $t^6 e^3 p^1 T_{1u}$. The corresponding $d-s$ transition, band II, is $t^6 e^3 s^1 E_g$. In neither case can we see evidence for transitions involving the $t^5 e^4$ configuration of the core.

There is, however, an indication of a transition involving the $t^5 e^4$ core in an interpretation of bands I and III. These bands could be transitions in Cu⁺ pairs, as suggested before, and their separation of 7800 cm^{-1} could reasonably be interpreted as the cubic-crystal-field splitting. Neighboring Cu⁺ ions form odd and even pairs of states. Transitions to the odd component are allowed, and would be temperature independent, as observed. A few observations of concentration dependence made by us, and those of Ref. 6, support the pair assignment. We have used $10Dq = 7800\text{ cm}^{-1}$ in the single-ion energy-level diagram shown in Fig. 3.

Additional information on the d^9p configuration of Cu⁺ in LiCl has been obtained by the observation of transitions from the metastable $t^6 e^3 s^3 E$ state to the triplets of $t^6 e^3 p$, and will be reported in another publication.

3d-4p transitions in transition-metal ions.

With the help of the data on LiCl:Cu⁺, we can suggest $3d-4p$ assignments for several other ions in crystal hosts.

The next most definite case that has come to our attention is that of V²⁺ in fluoride host crystals. This ion also has such a simple electron configuration that the number of excited state assignments is severely limited. The ground state of this $3d^3$ ion in an octahedral field is ${}^4A_{2g}(t_{2g}^3)$. The transition at $51\,000\text{ cm}^{-1}$ has been identified¹² as the $3d-4s$ band ${}^4A_{2g}(t_{2g}^3) \rightarrow {}^4T_2(t_{2g}^2 s)$. There are

no other levels in the $3d^2 4s$ manifold having quartet multiplicity which can be reached by a one-electron process from ${}^4A_{2g}(t_{2g}^3)$. Nevertheless, there is at least one, and probably two higher-energy absorption bands in LiF, the first at 1500 \AA , lying well below the lowest exciton band of the host crystal.⁵ This band is a possible $3d-4p$ transition, first, because of the lack of other obvious assignments and second, because of its various properties.

The properties which agree with the $3d-4p$ assignment are the following. The oscillator strength is about 6×10^{-3} , and therefore is about 10 times greater than for the $3d-4s$ transition. The oscillator strength does not increase with temperature. Both of these facts suggest that the transition is allowed. The transition energy shifts 600 cm^{-1} to higher energy in LiF and 400 cm^{-1} in KMgF₃ as the temperature is lowered from 300°K to about 5°K . This shift characterizes a transition localized on the ion, as it is the same behavior observed for a $3d-4s$ transition^{5,12} and is different from the behavior of anion-metal electron transfer transitions. The band shifts to higher energies in going from NaF to KMgF₃ to LiF as do the $3d-4s$ transitions,⁵ another characteristic of a transition localized on the metal ion.

We were reluctant to make the $3d-4p$ assignment for V²⁺ in fluorides because the transition energy would be much lower than in the free ion, whereas the $3d-4s$ transition energy is comparable to or higher than that of the free ion.^{5,12} The case of LiCl:Cu⁺, however, is quite similar to V²⁺ in that the $d-s$ interval increases while the $d-p$ interval decreases from free ion to solid. The energy-level diagrams of Cu⁺ and V²⁺ are compared in Fig. 3.

The $3d-4p$ interval in V²⁺ falls from $86\,000$ to $67\,000$ when the ion goes into LiF crystal. The crystal-field effect adds 6000 cm^{-1} of the $67\,000\text{ cm}^{-1}$ interval in the solid, so the interconfiguration shift caused by the solid is $25\,000\text{ cm}^{-1}$. For Cu⁺, this shift is from $72\,000$ to $58\,000$; without the crystal-field effect the latter would be $62\,000$ leaving a $10\,000\text{ cm}^{-1}$ interconfiguration shift. The smaller value for Cu⁺ is consistent with its lower ionic charge. Another well-established configuration shift is the $4f^{14} - 4f^{13} 5d$ transition energy of Yb²⁺, which is 6670 cm^{-1} toward lower energies when the ion is introduced into SrCl₂.¹⁷

The $3d^9 4p$ configurations of the free transition-metal ions are quite complex in some cases, but for V²⁺ and Cu⁺ all of the observed states having the same multiplicity as the ground state lie within 3000 cm^{-1} of each other.¹⁶ In the solid, the F and G parameters are reduced and all of these states

TABLE II. Free-ion values of $3d \rightarrow 4p$ transition and estimated values for fluoride host crystals.

	Transitions observed in crystal	Free ion ^a		C.F. ^b shift	Configuration shift	Calc. $d \rightarrow p$	Obs. $d \rightarrow p$
		Excited state	Transition energy				
V^{2+}	${}^4A_2(t^3) \rightarrow t^2({}^2T_1)p$	d^2p^4G	86	6.2	-25	(67)	67
Cr^{2+}	${}^5E(t^3e) \rightarrow t^3({}^4A_2)p$	d^3p^5G	94	-7.2	-27	60	59
Mn^{2+}	${}^6A_1(t^3e^2) \rightarrow t^3e({}^6E)p$	d^4p^6F	110	5.0	-29	76	(77)
Fe^{2+}	${}^3T_2(t^4e^2) \rightarrow t^3e^2({}^6A_1)p$	d^5p^5P	89	4.0	-31	62	(70)
Co^{2+}	${}^4T_1(t^5e^2) \rightarrow t^4e^2({}^6T_2)p$	d^6p^4D	107	2.0	-33	76	75
Ni^{2+}	${}^3A_2(t^6e^2) \rightarrow t^5e^2({}^4T_1)p$	d^7p^3G	116	4.4	-35	85	(~80)

^aTransition energy and other energy values are given in units of 1000 cm^{-1} .

^bC.F. is the crystal-field shift, see Ref. 12.

are expected to lie well within the bandwidth of the spectrum. In the case of V^{2+} we cannot see the $de_g \rightarrow pt_{1u}$ transition because de_g is not occupied in the ground state. Therefore, only one band of the $3d \rightarrow 4p$ type is expected for V^{2+} . Yet in this case, there does appear to be another high-energy band, at $78\,000 \text{ cm}^{-1}$, so that another type of transition must be occurring.

If the $3d \rightarrow 4p$ transition is now considered to have been identified in V^{2+} , it is possible to estimate the position of these bands in the other divalent transition metal ions. One can first assume that the same configuration shift of $24\,000 \text{ cm}^{-1}$ occurs in all of these $d \rightarrow p$ intervals, after including corrections for the d -shell splitting. These corrections are subtracted from the free ion value. For Cr^{2+} , the predicted $d \rightarrow p$ transition is $62\,000 \text{ cm}^{-1}$ while the observed band in KMgF_3 is at about $59\,000 \text{ cm}^{-1}$. There is a strong band at $75\,000 \text{ cm}^{-1}$ in Co^{2+} in LiF . If the latter is to be assigned to $3d \rightarrow 4p$, the configuration shift must be increased to $34\,000 \text{ cm}^{-1}$ for Co^{2+} . A linear shift with atomic number beginning at $25\,000 \text{ cm}^{-1}$ for V^{2+} and increasing by 2000 cm^{-1} for each successive atom fits the data, as we now know it, as shown in Table II.

The data in Table II are based on the three distinct strong bands found for V^{2+} (in LiF), Cr^{2+} (in KMgF_3), and Co^{2+} (in LiF). New data on Cr^{2+} in MgF_2 shows strong bands at $55\,000$ and $61\,000$.¹⁸ We expect these bands to shift to $\sim 63\,000 \text{ cm}^{-1}$ in LiF . The data for Mn^{2+} , Fe^{2+} , and Ni^{2+} are estimates of strongly absorbing regions in LiF or KMgF_3 , and do not represent distinct band peaks. The data for Fe^{2+} was difficult to interpret in Ref. 12, but there is no strong absorption until $70\,000 \text{ cm}^{-1}$, and this disagrees somewhat with the calculated value.

There is no previous body of knowledge with which to compare the $d^n \rightarrow d^{n-1}p$ configuration shifts. The approximate values taken in Table II are only crude estimates. A complete calculation of the

energies of the states of these configurations together with more experimental work will have to be done in order to interpret the spectra satisfactorily. Nevertheless, the agreement shown in this table supports the assignment of the $d \rightarrow p$ transitions.

It would be desirable to have theoretical descriptions of the $d^{n-1}p$ configurations in crystal fields. Shatwell has calculated oscillator strengths, ignoring configuration interaction, so as to find the relative strengths of the principal $d \rightarrow p$ bands of the transition-metal ions.¹⁹ These will be reported more fully in another publication, but the main results are these: The one-electron transitions from a t orbital to a p orbital have dipole strengths of $\frac{2}{5}\langle r \rangle^2$, while those from e orbitals have $\frac{4}{5}\langle r \rangle^2$, where $\langle r \rangle = \langle d || r || p \rangle$. Thus, the coupling conditions are not very important, and the changes in dipole strength from one ion to the next depend more on $\langle r \rangle^2$. This quantity of course is a parameter which depends on the actual nature of the d and p orbitals in the crystal, and it must change with both metal ion and host crystal. The observed differences in oscillator strength from one ion to the next are therefore not simply explainable but depend on the detailed nature of the p and d orbitals in the crystal.

Both the energy and intensity of the $d \rightarrow p$ bands should serve as experimental tests of calculated impurity-ion wave functions. These high energy levels which interact strongly with crystal levels should be interesting for future theoretical studies.

Loh has recently also identified some of the higher-energy bands of Refs. 5 and 12 as $d \rightarrow p$ transitions, using only the evidence of band positions and intensities.²⁰

ACKNOWLEDGMENT

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- ¹K. Fussganger, *Phys. Status Solidi* **34**, 157 (1969).
- ²K. Fussganger, *Phys. Status Solidi* **36**, 645 (1969).
- ³D. Bramanti, M. Mancini, and A. Runfagno, *Phys. Rev. B* **3**, 3670 (1971).
- ⁴A. Barry Kunz, *Phys. Rev. B* **2**, 5015 (1970).
- ⁵D. Bruce Chase and Donald S. McClure, *J. Chem. Phys.* **64**, 74 (1976).
- ⁶O. T. Antonyak, V. N. Vishnevskii, N. S. Pidzyrullo, and M. V. Tokarivskii, *Izv. Vysshelikh Uchebnykh Zavedenii Fizika* No. 8, 124-128 (1974).
- ⁷E. Kratzig, T. Timusk, and W. Martiensen, *Phys. Status Solidi* **10**, 709 (1965).
- ⁸R. L. Bateman, W. J. Van Sciver, *Phys. Status Solidi B* **46**, 779 (1971).
- ⁹*Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).
- ¹⁰R. Sittig, *Phys. Status Solidi* **24**, K189 (1969).
- ¹¹M. Piccirilli and G. Spinolo, *Phys. Rev. B* **4**, 1339 (1972).
- ¹²J. F. Sabatini, A. E. Salwin, and D. S. McClure, *Phys. Rev. B* **11**, 3832 (1975).
- ¹³Kwok Leung Yip and W. B. Fowler, *Phys. Status Solidi B* **53**, 137 (1972).
- ¹⁴T. Tsuboi (unpublished).
- ¹⁵R. Onaka, A. Fukuda, K. Inohara, T. Mabuchi, and Y. Fujioka, *Jpn. J. Appl. Phys.* **4**, Suppl. I (1965); *Proceedings of the Conference on Phot. and Spect. Opt.*, Kyoto and Tokyo, 1964 (unpublished); R. Onaka, S. Yano, and Y. Kondo, *Science of Light* **13**, 26 (1964).
- ¹⁶C. E. Moore, *Atomic Energy Levels*, U.S. Nat. Bur. DATA Ser. No. NBS (U.S. GPO, Washington, D.C., 1949); Vols. I and II.
- ¹⁷T. S. Piper, J. P. Brown, and D. S. McClure, *J. Chem. Phys.* **46**, 1353 (1967).
- ¹⁸A. E. Salwin (unpublished).
- ¹⁹R. A. Shatwell (unpublished).
- ²⁰E. Loh, *J. Phys. C* **10**, 1987 (1977).