

square law is to be valid. A mechanism in which color centers are not destroyed except by transformation to higher aggregates is shown to be inconsistent with the experimental data. Another mechanism involving both the creation and destruction of F and M centers solely by x rays is shown to be consistent with the square law if the probability of destroying a vacancy-electron complex is independent of whether the complex is isolated or associated with another complex. This mechanism is

consistent with experimental data presented on the production of F and M centers at liquid-nitrogen temperature by x rays in KCl.

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Vibronic Spectra of $\text{SrF}_2:\text{Sm}^{2+}$ and $\text{BaF}_2:\text{Sm}^{2+}$

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Recent work of Wood and Kaiser has yielded vibronic data on Sm^{2+} doped in two isomorphous crystals, SrF_2 and BaF_2 . The present work proposes a model using Born-von Karmann boundary conditions, which predicts the number of vibronic satellites and the $k=0$ selection rules. It is shown, however, that the $k=0$ selection rules are too restrictive to explain the vibronic spectrum and that to obtain a satisfactory explanation one must consider transitions involving vibrations away from $k=0$. The model, when such transitions are taken into account, is shown to be consistent with the observed data. It is proposed that one of the modes observed in the vibronic spectrum corresponds to vibrations of the transverse optical branch, a second to the longitudinal optical branch, and a third to transitions away from $k=0$ involving the Raman active branch. This model is able to qualitatively explain the differences observed in the two host lattices. It is contrasted with an XY_3 complex model, proposed by Axe and Sorokin to explain the same data. Raman scattering data have been obtained placing the F_{2g} mode (at $k=0$) at 280 cm^{-1} in SrF_2 and at 243 cm^{-1} in BaF_2 .

INTRODUCTION

THE spectra of lanthanide ions in crystals often display so-called vibronic satellites in addition to lines attributed to pure electronic transitions. These

vibronic lines are attributed to a simultaneous excitation of the lanthanide ion and a lattice vibration.¹ The evidence for such a conclusion is outlined in a recent publication² (hereafter referred to as RSW) and will not be covered here. What remains uncertain is the model appropriate to the analysis of such vibronic transitions. In this note it will be shown that a reasonable explanation of the data of Wood and Kaiser³ on Sm^{2+} in SrF_2 and BaF_2 is provided by the model of Born and von Karmann for the lattice modes, obtained in the manner of Hornig,⁴ and Winston and Halford.⁵ The application to vibronic transitions requires some modification of the methods of Hornig, and Winston and Halford, and these are outlined in RSW.

EXPERIMENTAL DATA

The fluorescence spectra of Sm^{2+} in SrF_2 and BaF_2 are given in Table I. The data are from Wood and Kaiser.³ The column labeled $\delta\nu$ gives the spacing of the vibronic satellites from its associated electronic transition. If the transition is electronic, then there is an e in this column. The labeling: "two phonon processes" indicates

TABLE I. Fluorescence spectra of Sm^{2+} in SrF_2 and BaF_2 .^a

SrF_2		BaF_2		SrF_2	
Energy (cm^{-1})	$\delta\nu$ (cm^{-1})	Energy (cm^{-1})	$\delta\nu$ (cm^{-1})	Energy (cm^{-1})	$\delta\nu$ (cm^{-1})
14 803		14 652	e	13 140	e
14 616	e	14 432	220	13 050	90
14 530	86	14 465	187	12 980	160
14 470	146	14 395	257	12 950	190
14 390	226	14 331	321	12 890	250
14 325	291			12 850	290
14 260	356			12 780	360
				12 580	560 ^c
14 353	e	14 374	e	12 550	590 ^d
14 125	228	14 186	188	12 520	620
14 060	293	14 118	256	12 470	670 ^e
13 955	358			12 450	690
13 964	e	13 943 ^b	e	12 350	e
13 870	94	13 755	188	12 276	74
13 800	164	13 689	254	12 246	104
13 750	214			12 146	204
13 680	284			12 096	254
13 625	339			12 016	334
13 581	e	13 620 ^b	e		
13 490	91	13 432	188		
13 450	131	13 364	256		
13 370	211				
13 290	291				
13 230	351				

^a The letter e means electronic transition.

^b Not observed but probably where indicated.

^c Two-phonon process: 2×280 .

^d Two-phonon process: $360 + 220$.

^e Two-phonon process: $360 + 290$.

¹ H. Ewald, *Ann. Physik* **34**, 209 (1939).

² I. Richman, R. A. Satten, and E. Y. Wong, *J. Chem. Phys.* **39**, 1833 (1963).

³ D. L. Wood and W. Kaiser, *Phys. Rev.* **126**, 2079 (1962).

⁴ D. F. Hornig, *J. Chem. Phys.* **16**, 1063 (1948).

⁵ H. Winston and W. Halford, *J. Chem. Phys.* **17**, 607 (1949).

the possibility of the vibrational level being the sum of two previously observed levels. The numbers can only be approximate and are not meant to be definite assignments. Although Wood and Kaiser also obtained data on $\text{CaF}_2:\text{Sm}^{2+}$, it is felt that the spectrum was too diffuse to obtain reliable vibronic transitions and therefore this discussion is limited to the SrF_2 and BaF_2 hosts.

The strong vibronic features in both hosts are pairs of lines associated with most electronic transitions. In $\text{BaF}_2:\text{Sm}^{2+}$ these pairs occur at 188 cm^{-1} and 256 cm^{-1} below the parent electronic transitions. In the SrF_2 host the corresponding lines lie at 220 cm^{-1} and 290 cm^{-1} below the associated electronic transitions. In the BaF_2 host there is also a vibronic satellite at $14\,331\text{ cm}^{-1}$ which is probably associated with the electronic transition at $14\,374\text{ cm}^{-1}$, yielding a vibrational level at 321 cm^{-1} . In the SrF_2 host there is a vibrational level which varies between 339 and 360 cm^{-1} , superimposed on several electronic transitions. There is also a vibrational level at about 90 cm^{-1} in this host which occurs coupled to several electronic transitions.

Wood and Kaiser show that the fluorescing level is ${}^5D_0 A_{1g}$. Infrared data of Kaiser *et al.*⁶ place the transverse optical modes at 217 cm^{-1} in SrF_2 , and at 184 cm^{-1} in BaF_2 . They also find in SrF_2 a 99 cm^{-1} level which they assign to an acoustic branch. In addition, using the Lyddane-Sachs-Teller⁷ formula, they predict the positions of the longitudinal optical branches to be 374 cm^{-1} for SrF_2 , and 326 cm^{-1} for BaF_2 .

Raman data were obtained by the author on single crystals of SrF_2 and BaF_2 placing the $k=0$ Raman active branch at 280 cm^{-1} in SrF_2 , and at 243 cm^{-1} in BaF_2 .

THEORY

The two host lattices are isomorphic and have face-centered cubic Bravais lattices. There is one molecule per primitive unit cell and the unit cell group⁴ is O_h . The symmetry imposed $k=0$ selection rules for one phonon vibronic transitions from an A_{1g} electronic excited state are readily obtained. At $k=0$ there are two vibrational levels besides the triply degenerate acoustic level. One transforms according to F_{1u} of the unit cell group and the other according to F_{2g} . The F_{1u} mode is infrared active, and the F_{2g} mode is Raman active. For electric dipole radiation F_{1u} modes may be coupled to transitions terminating on all electronic states except those transforming as A_{2g} or F_{1g} . F_{2g} modes cannot appear coupled to electronic transitions between states within a configuration.

The triply degenerate (at $k=0$) F_{1u} branch will be split near $k=0$ into longitudinal and transverse

branches. Since it has been shown in RSW that transitions at $k=0$ cannot alone account for observed vibronic intensities, one must include all k values in the analysis. This is reasonable when one takes into account the perturbations in the host lattice arising from the impurity ion, in which case one may expect deviations from the $k=0$ approximation and possibly the appearance of localized vibrations. One would therefore expect the F_{1u} branch to result in broad vibronic transitions which may be resolvable into two bands.

If the $k=0$ selection rules are no longer even approximately valid for those regions of a branch which have a high density of states, then one would expect these vibrations to also appear in vibronic transitions. This is so because there exist no symmetry-imposed selection rules for most regions of k space. Thus vibrations in the F_{2g} and acoustic branches away from $k=0$ may appear associated with electronic transitions.

DISCUSSION

The vibronic spectrum of $\text{BaF}_2:\text{Sm}^{2+}$ consists mainly of paired lines. One line of each pair corresponds to a vibration of the transverse infrared active branch coupled to an electronic transition, as pointed out by Wood and Kaiser. The second line involves a vibration whose energy is very close to that of the Raman mode. However, since such transitions are forbidden at $k=0$, one must assign this vibration to some region of the F_{2g} branch away from $k=0$ where the density of states is high. One vibronic transition in $\text{BaF}_2:\text{Sm}^{2+}$ involves a vibrational level at 321 cm^{-1} . This level is assigned to the longitudinal infrared active branch because its energy is very close to that predicted for it by Kaiser *et al.*⁶

The vibronic spectrum of $\text{SrF}_2:\text{Sm}^{2+}$ is somewhat more difficult to analyze. This is probably because of the difference in mass and electronic structure between Sr^{2+} and Sm^{2+} as contrasted with the similarity between Ba^{2+} and Sm^{2+} . Such a difference would be expected to shift the lattice vibration frequencies in the doped crystal away from those in the pure host for those vibrations which are somewhat localized near the impurity. Vibronic transitions must involve such localized vibrations. Taking into account the possibility of shifts from the pure host, and making use of the strong similarity between the vibronic spectra in the two hosts, the following assignments have been made. The 90 cm^{-1} vibration is assigned to an acoustic branch as indicated by Kaiser *et al.* The 220 cm^{-1} vibration is assigned to the transverse infrared active branch in agreement with Wood and Kaiser. The 290 cm^{-1} vibration is assigned to transitions away from $k=0$ involving the Raman active branch. The vibronic transitions associated with vibrations at about 350 cm^{-1} are probably the result of excitation of vibrations in the longitudinal branch together with an electronic transition. In the pure host the predicted energy of this

⁶ W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, *Phys. Rev.* **127**, 1950 (1962).

⁷ R. Lyddane, R. G. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).

branch is 374 cm^{-1} .⁶ The introduction of the impurity ion may explain the general shift toward lower energy in the doped crystal.

The $\text{SrF}_2:\text{Sm}^{2+}$ vibronic spectrum also yields a vibrational yield at about 140 cm^{-1} . This may be an acoustic mode but there is insufficient data to make an assignment.

Axe and Sorokin,⁸ using the data of Wood and Kaiser, also made an analysis of the vibronic levels in these two crystals. They assumed an XY_8 complex in analogy with the work of Satten *et al.*^{9,10} However, Satten's work on the UCl_6^{2-} complex showed that the U^{4+} is tightly bound in the complex and interacts mainly with the inner vibrations of this complex. No such complex would be expected in the strongly ionic crystals under consideration here.

⁸ J. D. Axe and P. P. Sorokin, *Phys. Rev.* **130**, 945 (1963).

⁹ R. A. Satten, *J. Chem. Phys.* **29**, 658 (1958).

¹⁰ S. A. Pollack and R. A. Satten, *J. Chem. Phys.* **36**, 804 (1962).

CONCLUSION

It has been shown that a model taking into account vibrations of the entire lattice is able to explain most of the vibronic features observed in $\text{SrF}_2:\text{Sm}^{2+}$ and $\text{BaF}_2:\text{Sm}^{2+}$. A model based only on the $k=0$ modes results in fewer transitions than are observed and therefore cannot be correct. An XY_8 complex model is not able to explain as many of the details of the vibronic spectra as simply as does the one presented here, and, in any case, would not be expected to be a reasonable approximation for these crystals.

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Polarization Effects in Slow Neutron Scattering II. Spin-Orbit Scattering and Interference*

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The theory of polarized neutron scattering is extended to include spin-orbit scattering in magnetic substances. The cross section for scattering of a polarized beam includes, in addition to the Schwinger interference term between nuclear and spin-orbit scattering, a polarization-dependent interference term between spin-orbit and magnetic scattering. The latter depends on the real part of the product of magnetic and spin-orbit structure factors, whereas the Schwinger term depends on the imaginary part of the product of the nuclear and spin-orbit structure factors. A calculation shows that this effect should easily be observable in an isotopic mixture of Ni which has no coherent nuclear scattering.

INTRODUCTION

IN a recent experiment, Shull¹ has detected the spin-orbit scattering of slow neutrons. This type of scattering was first discussed by Schwinger² in connection with the polarization of fast neutron beams. It has since been considered by a number of other authors³ who have calculated higher order corrections to the Schwinger expression, in the hope of distinguishing these effects from those of the polarizability of the meson cloud of the neutron.

The Schwinger scattering, as measured by Shull, is due to interference between the nuclear and spin-orbit scattering. Because the spin-orbit scattering amplitude

is imaginary, this interference term depends on the imaginary part of the nuclear scattering amplitude. In this paper it is shown that in the scattering of neutrons by magnetic substances an interference phenomenon occurs between spin-orbit and magnetic scattering which depends on the real part of the magnetic scattering amplitude. This polarization-dependent term provides an alternate method for the measurement of the spin-orbit scattering amplitude.

The principal interactions of a slow neutron with a solid are the nuclear interaction with the nuclei of the atoms and, in magnetic substances, the interaction of the neutron's magnetic moment with the spin and orbital magnetic moments of the atomic electrons. In addition to these there are a number of others which have, for thermal neutrons, scattering amplitudes of the order of 10^{-3} of the above nuclear and magnetic interactions. These are the magnetic neutron dipole-nuclear dipole interaction, the specific neutron-electron

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¹ C. G. Shull, *Phys. Rev. Letters* **10**, 297 (1963).

² J. Schwinger, *Phys. Rev.* **73**, 407 (1948).

³ S. B. Gerasimov, A. I. Lebedev, and V. A. Petrun'kin, *Zh. Eksperim. i Teor. Fiz.* **43**, 1872 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 1321 (1963)], and other references contained therein.