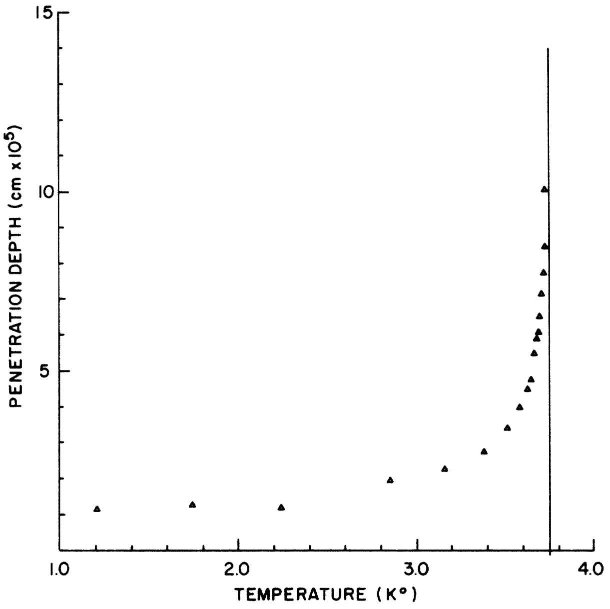

FIG. 1. Penetration depth λ as a function of temperature for a 350Å tin film. ($T_c = 3.755$°K.)

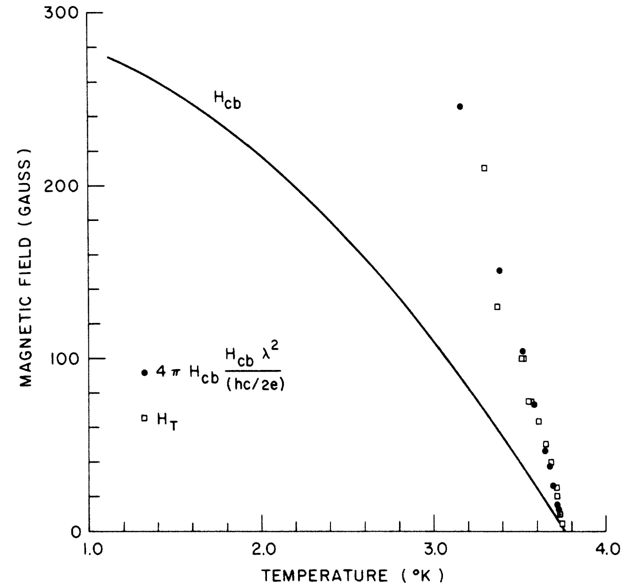

FIG. 2. Critical field as a function of temperature. Experimental confirmation is indicated by the complete overlap of the data points for measured H_T (open squares) and calculated values (solid circles). H_{cb} denotes the bulk critical field.

tal points. Notice especially this critical field is nearly three times the bulk critical field. Equally satisfactory results have been obtained for 300Å and 750Å films. For these films, the penetration depth differs in magnitude but conforms well to the expected size effect.[5] In the 300Å film, the penetration depth λ, and thus H_T, is slightly larger while in the 750Å film, the penetration depth λ is smaller and in this case H_T is slightly less than H_{cb}.

These data seem to confirm the self-consistency of Tinkham's analysis with no adjustments and lend support to the assumption of flux penetration in units of $hc/2e$ through thin mechanically singly connected superconductors.

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[1] M. Tinkham, Phys. Rev. 129, 2413 (1963).

[2] J. E. Mercereau and L. T. Crane, Phys. Rev. Letters 9, 381 (1962).

[3] Details to be reported. See also A. L. Schawlow, Phys. Rev. 109, 1856 (1958).

[4] J. Bardeen and J. R. Schrieffer, in Progress in Low-Temperature Physics, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, Chap. 6.

[5] M. Tinkham, Phys. Rev. 110, 26 (1958).

VIBRONICS IN GADOLINIUM COMPOUNDS*

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Vibronic (vibroelectronic) structure of electronic transitions occurs often in the spectra of rare-earth ions in crystals.[1] The intensity of these lines in the absorption spectra of praseodymium or neodymium salts is as strong as that of the pure electronic transitions.[2]

There is a distinction between vibronic transitions involving "external" or "internal" vibrations. The former involve a lattice mode in which the rare-earth (RE) ion actually participates. An "internal" vibration corresponds to an internal motion of a molecular group in the crystal. This can often be correlated to a corresponding vibration of the molecule in the gaseous phase. There is no evidence that the RE ion participates in an "internal" vibration.

Table I. Emission and absorption vibronics.

		Fluorescence		Absorption			
Compound	Gd^{3+} parent transition (Å)	Vibronic transition (Å)	Vibration frequency (cm^{-1})	Vibronic transition (Å)	Vibration frequency (cm^{-1})	Molecular group	Infrared or Raman frequency (cm^{-1})[a]
$GdCl_3 \cdot (6H_2O)$	3118	3281	1590	2820	3390	H_2O	1650
		3480	3330				3210
$GdCl_3 \cdot (6D_2O)$	3118	3238	1190	2886	2580	D_2O	1220
		3377	2460				2512
$Gd_2(SO_4)_3 \cdot (8H_2O)$	3117	3227	1080			SO_4	1105
		3284	1630			H_2O	1650
		3480	3345				3210
$Gd_2(SeO_4)_3 \cdot 8H_2O$	3120	3207	870			SeO_4	875
		3483	3340			H_2O	3210
$Gd[(C_2H_5)SO_4]_3 \cdot (9H_2O)$	3112	3233	1200			SO_4	1105
		3280	1640			H_2O	1650
		3478	3380				3210
$GdPO_4$	3117	3233	1200			PO_4	1080

[a] H. H. Landolt and R. Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, edited by R. Meche and F. Kerkhof (Springer-Verlag, Berlin, 1951), Vol. I, Part 2.

In a recent investigation of the fluorescence and absorption of gadolinium compounds, a number of "internal" vibronics were observed. The transitions are compiled in Table I. The wavelengths were determined from low-resolution (16Å/mm) spectrograms obtained by a Bausch and Lomb grating monochromator. A typical spectrogram of $GdCl_3 \cdot 6D_2O$ is reproduced in Fig. 1. It is seen that the widths of the unresolved groups of Stark lines do not permit an accuracy better than a few angstroms. The emitted vibronics were of a longer wavelength than the strong parent electronic emission group at 3118 Å. Similar transitions were found in the absorption spectra of the two chlorides at the same energy distance to the short-wavelength side of the parent transition. Such lines were found also at wavelengths expected for vibronics in the other crystals but their assignment was uncertain.

Tomaschek[3] has observed emission lines corresponding to the vibronics in $Gd_2(SO_4)_3 \cdot 8H_2O$. He did not discuss their nature probably because the electronic levels were not known well enough at that time.

Gadolinium is particularly favorable for studying emission vibronics since its energy level scheme does not yield emission lines longer than 3118 Å.[4] Thus, lines observed at longer wave-

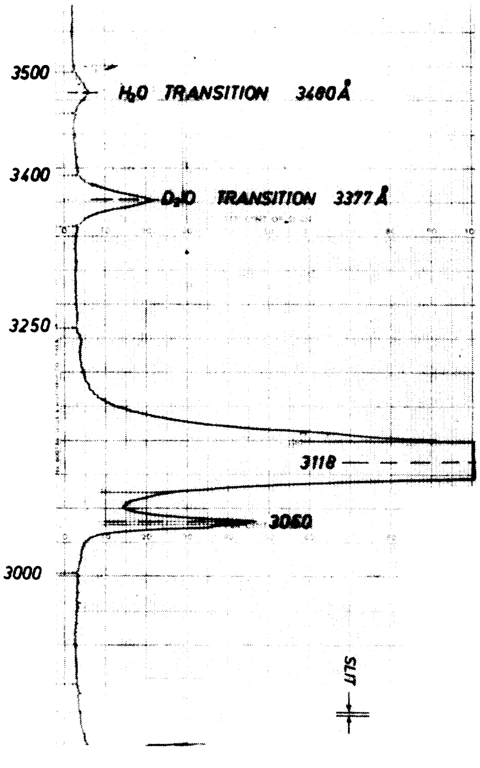

FIG. 1. Fluorescence spectrum of $GdCl_36D_3O$ (+ trace H_2O).

lengths are either vibronics or impurity effects. The latter alternative was ruled out by the following observations:

(a) In each of the investigated crystals there is a close fit between the decay time of the electronic parent transition (3118 Å) and those of the accompanying vibronics. This is an indication that the lines are emitted from the same level.

(b) In each case, the frequency difference between the parent and a particular vibronic closely matches the vibration frequency of a molecular group in the vicinity of the emitting ion. This is illustrated in columns four and eight of the table where the vibration frequencies can be compared with infrared data.

(c) The frequencies of the absorption vibronics appear as a mirror image of the emission vibronic frequencies with respect to the parent transitions.

We believe that similar results can be obtained in other gadolinium compounds. The emission vibronics will appear if the parent transition is strong in fluorescence.[5] One would also expect a similar vibronic structure in the corresponding compounds of Sm, Eu, Tb, and Dy. The assignment of emission vibronics in these ions is more difficult because of the possible proximity of pure electronic transitions.

The mechanism and selection rules of the "internal" vibronics are not well understood.[6] K. H. Hellwege[1] discussed a model in which the interaction between the RE ion and the molecular groups is not introduced explicitly. Our results indicate that there is a strong similarity between the transition of "internal" vibronics and the recently discovered cooperative absorption in RE ions.[7] Dexter[8] has developed a model for this absorption which is dependent on the interaction between pairs of ions. This model is applicable to the internal vibronics as well.[9]

According to such treatment the relative intensity of a cooperative ion-molecule transition increases with the strength of transition between neighboring vibrational states of the molecular group (infrared activity).

The gadolinium vibronics of highest intensity which have been observed correspond to vibrations which are strongly infrared active as expected.

The final state of a vibronic emission in gadolinium consists of a Gd ion in the ground state, a molecular group in the first excited vibrational level, and the radiation field gaining a photon of the vibronic frequency. The inverse process involves the absorption of both a photon and a phonon to excite the Gd ion from its ground state. At room temperature (or lower) the excited vibration states of the frequencies in column four of Table I are practically unoccupied. Therefore, the probability of reabsorption of such vibronic photons is low. Thus, the system is essentially a four-level scheme and as such is of interest for stimulated emission studies. Further work on linewidths and relative intensities is needed to determine threshold conditions for induced emission in these lines.

Our thanks are extended to Professor W. Low for his encouragement in this work.

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[1] A. M. Hellwege and K. H. Hellwege, Z. Physik 133, 176 (1952); and references therein.

[2] K. H. Hellwege, Ann. Physik 40, 529 (1941).

[3] R. Tomaschek, Ann. Physik 29, 306 (1937).

[4] This does not exclude possible observations of infrared radiation between excited states.

[5] A notable example of a reluctant crystal is Gd nitrate.

[6] J. P. Mathieu, Ann. Phys. (Paris) 5, 379 (1950).

[7] F. Varsanyi and G. H. Dieke, Phys. Rev. Letters 7, 442 (1961).

[8] D. L. Dexter, Phys. Rev. 126, 1962 (1962).

[9] S. Yatsiv (to be published).

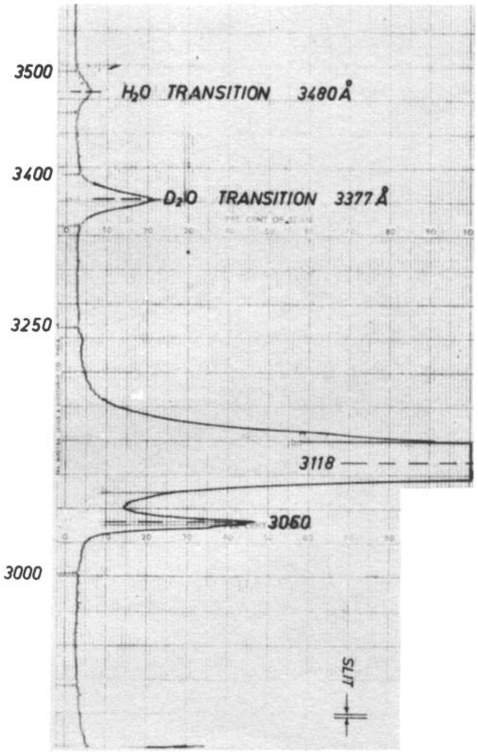

FIG. 1. Fluorescence spectrum of $GdCl_36D_3O$ (+ trace H_2O).