Motors Research Laboratories for a gift of single crystals of CdS.

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[1] J. Lambe and R. Ager, Rev. Sci. Instr. 30, 599 (1959).

[2] L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids 1, 117 (1956); C. Kikuchi, Phys. Rev. 100, 1243 (1955).

ELECTRONIC SPECTRA OF EXCHANGE-COUPLED ION PAIRS IN CRYSTALS

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Trivalent chromium ions (Cr^{3+}) in many insulating crystal lattices fluoresce with the emission of sharp lines near 7000 angstroms. The strongest emission lines in this region are well understood from crystal field theory as transitions from a ^2E excited state to the $^4A_2$ ground state.[1] In MgO there is one ^2E line since in a strictly cubic field the degeneracy of the upper level is not split. In ruby (Al_2O_3), however, there are two ^2E lines due to the lifting of the upper level degeneracy by the trigonal component of the crystal field. The ground state is also split in ruby, but by a much smaller amount which is not usually resolved in the optical spectrum.

It has been known for many years that within a few hundred cm^{-1} of the ^2E lines there are other sharp lines and bands which are not accounted for by the crystal field theory.[2,3] It has been suggested[2,4] that these "satellites" are caused by transitions to excited lattice vibrational states, followed by the emission of a phonon, and this is probably correct for the broader band satellites. This suggestion does not fit the observations for the sharp lines, since at 4.2°K the satellite lines have different spacing in emission from those in absorption and the crossover point between absorption and emission does not coincide with the ^2E lines. One would expect the same satellite spacings in both emission and absorption, since the vibrational frequencies are a property of the host lattice, which is not changed by the electronic transition within the impurity atom. Vibrations of the O-Cr-O complex, which would change with excitation of the chromium ion, would not have frequencies less than 80 cm^{-1} from the crossover point.

We wish to propose that the satellite lines are not due to individual chromium ions, but to chromium ions paired with a neighboring chromium ion or with some other crystal defect. If the concentration of chromium is, say, 1 atomic percent, there is a probability varying from 3 % to 12 % depending on the local symmetry that a given ion will find another Cr^{3+} ion among its nearest neighbors. If there is any clustering of chromium ions, this probability will be still greater. Between such neighboring ions there will be strong exchange forces. Indeed, the exchange forces lead to antiferromagnetism in Cr_2O_3.

If the satellite lines are due to randomly distributed nearest neighbor pairs, at low concentrations of Cr^{3+} their intensity relative to the main lines should be proportional to the concentration. As shown in Fig. 1, this behavior has been observed in the fluorescence spectrum of ruby. At very low concentrations the satellites are vanish-

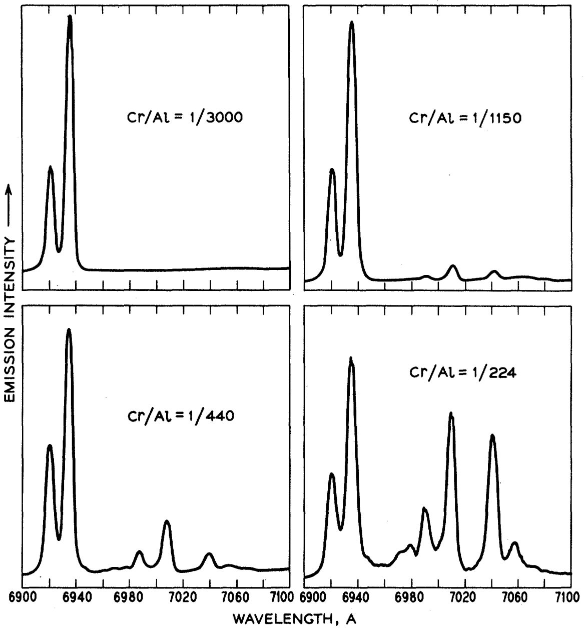

FIG. 1. Fluorescence spectrum of ruby at 77°K with different chromium concentrations (photoelectric recording at low resolution).

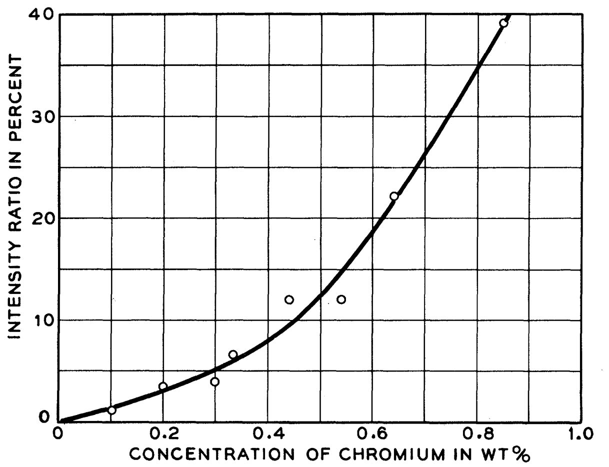

FIG. 2. Intensity ratio of strongest satellite (7010 A) to main line (6934 A) in ruby as a function of chromium concentration.

ingly faint, while at about 1% Cr^{3+}, they approach the main lines in intensity. In Fig. 2 the ratio of intensity for the strongest satellite (7010 A) relative to that of the main line is plotted against concentration. The curve shows a linear increase in the ratio at first, but then a faster rise. This may be due to the fact that pairs may remove the excitation from isolated atoms, since the lowest excited pair state lies lower than the corresponding state of the isolated atom.

The basis on which these spectra are being analyzed may be summarized briefly as follows: Ignoring the very small ground-state splitting, we may consider each chromium ion of a pair to be in a fourfold degenerate state of spin 3/2. The interactions between the spins will be represented by a Hamiltonian

$$H = 2J\vec{S}_1\cdot\vec{S}_2 + J_x S_{1x} S_{2x} + J_y S_{1y} S_{2y} + J_z S_{1z} S_{2z},$$

with $J_x + J_y + J_z = 0$.[5,6] The observed Curie-Weiss Θ of the homologous compound Cr$_2$O$_3$ is 1070°K,[7] which corresponds to a value of J equal to 50 cm^{-1} and an exchange field of 3×10^6 oersteds. Measurements[8] of the paramagnetic resonance line width in Cr$_2$O$_3$ above its Curie point yield a value of about 1000 oersteds. If the usual formula for exchange-narrowed line width[9] is applied, we see that the ratio of the anisotropic exchange terms J_x, J_y, J_z above to the isotropic term J cannot be larger than 10^{-2}. We propose initially to ignore these terms. The isotropic coupling term will then split the ground state into terms of total spin $S = 3, 2, 1, 0$.

Consider now the excited state where one ion of a chromium pair has been excited into the ^2E state. In MgO, this ion may be considered as occupying two degenerate states of spin 1/2, each of which will also be coupled by exchange to the ground state of the second ion. The excited state will then be split into two terms of total spin 2 or 1. If J is positive, the excited state $S = 1$ will lie lower than $S = 2$ and at sufficiently low temperatures will be the only one populated. It will be observed to fluoresce into the ground states of $S = 2$, 1, and 0, observing the selection rule $\Delta S = 0, \pm 1$. If J is negative, there will also be three possible lines. A calculation has been made of the intensity of these transitions and will be reported later.

In the case of Al$_2$O$_3$ an exact analysis of the observed spectrum has not yet been achieved, probably for the following reasons. The ^2E state is split by the combined action of spin-orbit coupling and the axial field. If the splitting were much larger than the exchange energy, the analysis of the pair states would be simple. In fact, the axial splitting and exchange are comparable, which complicates the interpretation of this spectrum. The analysis of the ruby spectrum is also made difficult by the existence of several nonequivalent types of chromium pairs.

In MgO, the Cr^{3+} fluorescence shows two groups of satellite lines, one of which varies with concentration somewhat like those of ruby. The other group persists to fairly low concentrations, and may be caused by selective pairing of a Cr^{3+} ion with whatever compensates the excess charge.[10,11] Since a large fraction of the chromium ions have their charge compensation nearby, it may be relatively rare for two uncompensated chromium ions to be near neighbors. Thus this spectrum involves the various kinds of charge compensation as well as chromium exchange interactions.

Efforts are continuing to obtain a detailed interpretation of the observed fluorescence spectrum and to study spectra produced by pairs of dissimilar atoms.

We wish to thank Professor G. H. Dieke for allowing us to see Jacobs' unpublished thesis. We also wish to thank A. D. Liehr and M. Peter for helpful discussions, and G. E. Devlin for assistance with the experiments. We are indebted to Miss S. M. Vincent for determining the chromium concentration by the method of x-ray

fluorescence.

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[1] S. Sugano and Y. Tanabe, J. Phys. Soc. (Japan) 9, 766 (1954).

[2] O. Deutschbein, Ann. Physik 14, 712 (1932); 20, 828 (1934).

[3] S. F. Jacobs, thesis, Johns Hopkins University, Baltimore, 1957 (unpublished).

[4] R. S. Krishnan, Proc. Indian Acad. Sci. A26, 450 (1947).

[5] J. M. Baker and B. Bleaney, Paris Conference on Low-Temperature Physics, 1955 (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956).

[6] Griffiths, Owen, Park, and Partridge, Phys. Rev. 108, 1345 (1957).

[7] L. R. Maxwell and T. R. McGuire, Revs. Modern Phys. 25, 279 (1953).

[8] Nagamiya, Yosida, and Kubo, Advances in Physics, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 14.

[9] P. W. Anderson and P. R. Weiss, Revs. Modern Phys. 25, 269 (1953).

[10] J. E. Wertz and P. Auzins, Phys. Rev. 106, 484 (1957).

[11] J. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) 73, 948 (1959).

PARAMAGNETIC RESONANCE DETECTION OF THE OPTICAL EXCITATION OF AN INFRARED STIMULABLE PHOSPHOR

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The effect of the optical excitation of a phosphor may in certain cases manifest itself by a change in the paramagnetic resonance spectrum of the phosphor. Attempts to observe such changes in inorganic phosphors have previously been made by Hershberger[1] and Low[2] without success. This Letter describes an experiment in which paramagnetic resonance absorption was used to observe the optical excitation of the infrared stimulable phosphor SrS:Eu, Sm.

The physical properties of this phosphor have been widely investigated, the most extensive investigations being those carried out by Keller et al.[3] One of the properties of this phosphor is its ability to store energy when optically excited with ultraviolet or blue radiation. This stored energy may subsequently be released by irradiation with either infrared (970 mμ) or orange (590 mμ) wavelengths.

A simplified band-theory model was proposed by Keller[3] to explain this and other properties of SrS:Eu, Sm. In brief, europium is present in the SrS lattice as Eu^{2+} and samarium as Sm^{3+}. Excitation by ultraviolet radiation corresponds to SrS base absorption with the formation of an electron-hole pair. The electron is subsequently trapped by the Sm^{3+} which becomes Sm^{2+} and the hole trapped at the europium site giving Eu^{3+}. Excitation by blue radiation results in a direct ionization of Eu^{2+} to Eu^{3+} with the electron subsequently being trapped by the Sm^{3+} site. In the case of either ultraviolet or blue excitation the net effect is to change Eu^{2+} to Eu^{3+} and Sm^{3+} to Sm^{2+}. The Eu^{2+} has an ${}^8S_{7/2}$ ground state which is paramagnetic.[2] The Eu^{3+} ground state is ${}^7F_0$ and is nonmagnetic. Excitation of this phosphor should therefore manifest itself by a diminution in the Eu^{2+} paramagnetic spectrum.

The stored energy may be exhausted by irradiating with the wavelength which removes an electron from the Sm^{2+} site to the conduction band. The Sm^{2+} may be ionized in two ways and hence there are two wavelengths, 970 mμ and 590 mμ, that may be used.[3]

A diminution in the magnitude of the Eu^{2+} paramagnetic spectrum when optically excited has been observed for a SrS:Eu, Sm phosphor of the following composition: SrS, 6% $SrSO_4$, 6% CaF_2, 0.02% Eu, and 0.02% Sm. The percentages are in terms of molar percent. The preparation has been described in reference 3. A Varian Associates 4500 EPR spectrometer was used. The rectangular cavity that was used operated in the TE_{102} mode and had one end removed and replaced with a stainless steel screen, 96×96 mesh, which allowed light to irradiate the sample in the cavity. The powder sample was mounted on a 0.9- by 0.4-inch Teflon button placed along the region of maximum H_1 field at the middle of the cavity. An Osram xenon arc lamp *XBO* 1001 combined with a Bausch and Lomb 33-86-40 grating monochromator were used to irradiate the sample. All measurements were made at room temperature.

A plot of the relative stored energy against wavelength of the exciting light was made in the