at T_N, becoming smaller as the specimen is reduced in size.[2] Secondly, strains, chemical impurities, and other lattice defects may be expected to cause local variations in the strengths of the interactions among magnetic ions. Different regions in the specimen would thus transform to the antiferromagnetic state at slightly different temperatures causing a broadening of the observed heat-capacity anomaly.

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ENERGY TRANSFER FROM 3*d* TO 4*f* ELECTRONS IN $LaAlO_3$:Cr, Nd

J. Murphy, R. C. Ohlmann, and R. Mazelsky
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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We have observed transfer of energy between the 3*d* levels of Cr^{3+} and the 4*f* levels of Nd^{3+} in $LaAlO_3$. Evidence for transfer is the observation of Nd^{3+} fluorescence when the wavelength of the exciting light falls in a region where only Cr^{3+} absorbs. $LaAlO_3$ is an excellent host for studying cooperative effects between rare-earth and transition-metal ions since both types may be substitutionally incorporated over large ranges of concentrations. The absorption and fluorescence spectra of both Cr^{3+} and Nd^{3+} separately in single crystals of $LaAlO_3$ have been reported.[1,2]

The intensive investigation of the optical spectra of rare earths in ionic crystals has revealed the occurrence of energy transfer between the 4*f* electrons of ion pairs.[3-6] In this Letter we report the preliminary results on the resonance energy transfer between Cr^{3+} and Nd^{3+}. Transfer from Mn^{2+} to Nd^{3+} in glass has been reported by Melamed.[7] Very weak Nd fluorescence has been reported when pumping into the Cr absorption bands of mixed powders of ruby and Nd_2O_3.[8]

Powder samples of $La_{1-x}Nd_xAl_{1-y}Cr_yO_3$ were prepared by reacting the dried oxides,[9] La_2O_3, Al_2O_3, Nd_2O_3, and Cr_2O_3, intimately mixed in proper proportion, and firing at 1450 °C for 36 hours, with remixing after 18 hours. Examination of the product by x-ray powder diffraction techniques reveals single-phase $LaAlO_3$ within the limits of the sensitivity of the method. The values of x used were 0, 0.0005, 0.005, 0.01, 0.02, and 0.05, and those of y were 0, 0.0005, 0.001, 0.005, and 0.01.

Fluorescence spectra at 1Å resolution were obtained using a one-meter Jarrell-Ash Co. spectrometer and a cooled RCA 7102 photomultiplier, the samples being excited by an AH-6 mercury lamp with filtering by $CuSO_4$ solution. Excitation spectra at 100Å resolution were measured by exciting the sample with monochromatic light from a tungsten lamp filtered by a Farrand grating monochromator. In order to reduce the excitation spectra to the basis of constant incident quanta, the wavelength dependence of the quantal output of the Farrand monochromator was measured using a calibrated photomultiplier. In the excitation studies the fluorescence of Nd^{3+} was isolated using a Wratten No. 87C filter in front of the RCA 7102 photomultiplier, while Cr^{3+} fluorescence was isolated with a Wratten No. 88A filter in front of an RCA 7265 photomultiplier.

The room-temperature fluorescence spectrum, covering the region from 0.7 to 1.1 μ, of a powder

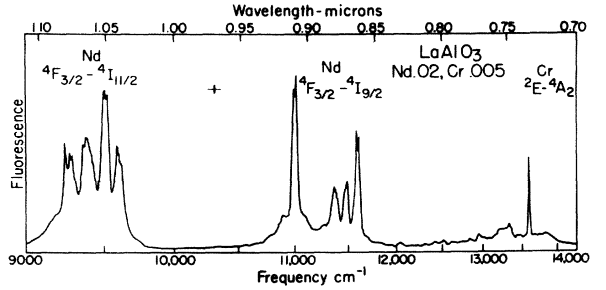

FIG. 1. Fluorescence spectrum of $LaAlO_3$:Cr, Nd excited with a high-pressure mercury lamp. The relative intensities of the Cr^{3+} and Nd^{3+} emission are not significant.

containing 2% Nd and 0.5% Cr is shown in Fig. 1. The line at 7356 Å and the structure around it are due to Cr^{3+}. The remaining two groups are associated with the fluorescence of Nd^{3+}. The spectrum is a superposition of the spectra for the samples containing only Cr^{3+} (0.5%)[1,2] and only Nd^{3+} (2%).[1] The relative intensities of the Nd^{3+} and Cr^{3+} groups shown in Fig. 1 are not significant since the spectral output of the AH-6 lamp favors the Cr^{3+} absorption bands.

Figure 2 shows the excitation spectra of the Cr^{3+} and Nd^{3+} fluorescence in samples containing 0.5% Cr^{3+} and/or 2% Nd^{3+}. The two excitation bands for the Cr^{3+} fluorescence correspond to the absorptions involving transitions from the $^4A_2$ to the $^4T_2$ and $^4T_1$ states. In the samples containing both Cr and Nd the Cr^{3+} excitation spectrum is identical with that shown. However, the intensity of the Cr^{3+} fluorescence decreases rapidly with increasing Nd concentration, being reduced by a factor of about 20 at 2% Nd concentration. There is no evidence therefore for transfer from Nd^{3+} to Cr^{3+}.

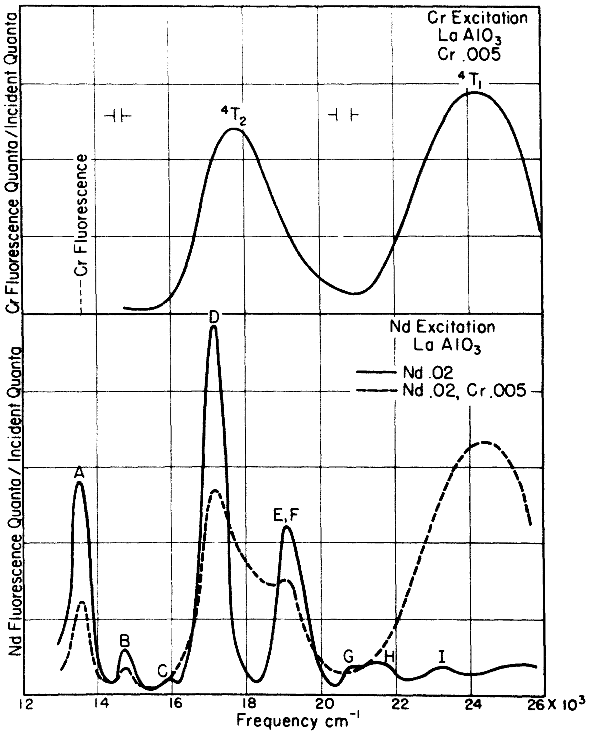

FIG. 2. Excitation spectra of Cr^{3+} emission (upper curve) and Nd^{3+} emission (lower curves). The ordinates for the upper and lower curves are not to the same scale.

The excitation spectrum for Nd^{3+} fluorescence in the absence of Cr^{3+} is shown by the solid curve in the lower part of Fig. 2. The peaks in the spectrum correspond to the transitions to the excited states of Nd^{3+} and are labelled in accordance with Dieke and Crosswhite.[10] The dashed curve is the excitation spectrum of a sample containing both Nd and Cr. There is clear evidence for transfer of energy from Cr^{3+} to Nd^{3+}. A reduction in the Nd^{3+} fluorescence intensity for excitation in the regions of Nd^{3+} absorption (*A* to *F* in Fig. 2) also occurs whenever Cr^3 is present in the sample.

The room-temperature decay time of the Nd^{3+} fluorescence (~460 μsec) does not change when Cr^{3+} is included in the sample. The decay of the Cr^{3+} fluorescence around 7356 Å involves a sum of exponentials. The longest decay time is 46 msec at room temperature[2] and is associated with the main line (*R* line). The presence of Nd^{3+} does not produce any significant change in the measured *R*-line lifetime.

The energy-level diagrams for Cr^{3+} and Nd^{3+} in $LaAlO_3$ as determined from the room-temperature fluorescence and excitation spectra are illustrated in Fig. 3. The structure on the Cr^{3+} levels represents vibronic states.

Since the spectral distribution of the Cr^{3+} fluorescence including the vibronic bands has not been observed to vary with the addition of Nd^{3+}, we infer that the energy transfer does not involve the emission and reabsorption of photons, i.e., no radiative transfer.

Nonradiative energy transfer involving a resonance between the electronic states of two ions has been discussed by Forster[11] and by Dexter.[12] Figure 3 shows that there are several possibilities for resonance transfer in the Cr^{3+}, Nd^{3+} system. We assume that relaxation of the lattice about the Cr^{3+} ions occurs very rapidly so that any emission or transfer originates from the bottom of the Cr^{3+} bands.

The transfer most likely involves a dipole-di-

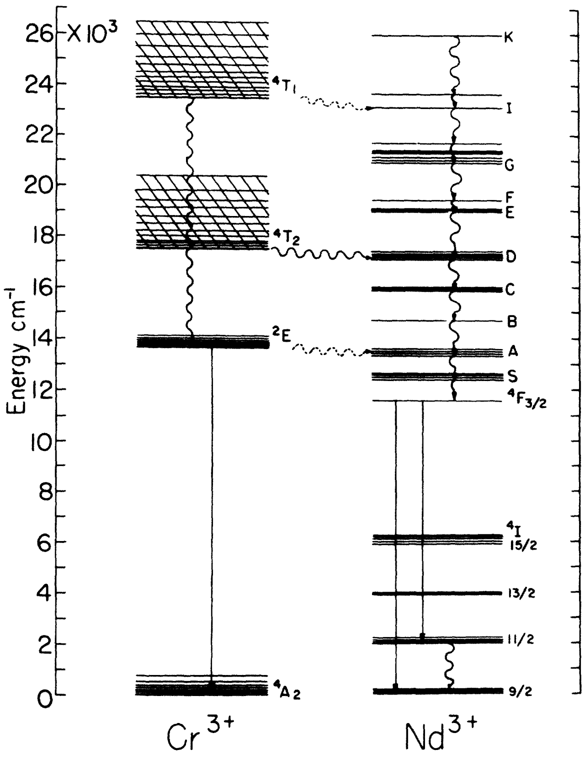

FIG. 3. Energy levels of Cr^{3+} and Nd^{3+} in $LaAlO_3$.

pole or dipole-quadrupole interaction since it has been observed in samples containing as little as 0.05 at. % Nd^{3+} with 0.5 at. % Cr^{3+}. Exchange effects should not contribute at these concentrations provided the ions are distributed randomly throughout the lattice. The magnitude of the matrix elements of the interaction Hamiltonian are proportional to the absorption and emission strengths of the separate ions.[12] It is probable that the transfer occurs between the $^4T_2$ level of Cr^{3+} and the D levels of Nd^{3+} since it is only for this resonance that both ions have relatively large oscillator strengths.

The fact that the lifetime of the R-line emission of Cr^{3+} does not change when Nd^{3+} is present supports the conclusion that transfer occurs from the $^4T_2$ level and that transfer from the ^2E level is not important. We could not test whether any transfer occurs from the ^2E state of Cr^{3+} by exciting this level directly since the transition probability for $^2E \leftarrow {}^2A$ is too small for observable absorption to occur in our samples.

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