Observation of Antiresonances in Fluorescence Spectra of Cr^{+3} and Nd^{+3} Doped Glasses

W. Stręk, E. Łukowiak, and
B. Jeżowska-Trzebiatowska

Institute for Low Temperature and Structure Research,
Polish Academy of Sciences, Wrocław, Poland

Z. Naturforsch. **38 a,** 587 – 588 (1983);
received December 11, 1982

The fluorescence spectra of Cr^{+3} in the presence of Nd^{+3} in glasses were studied. The "dips" observed in the spectra are interpreted as antiresonances due to Cr-Nd interaction.

Introduction

According to Fano's theory [1, 2] the interaction of a discrete autoionized state with a continuum manifests itself in antiresonance peaks in the excitation spectra. Sturge, Guggenheim and Pryce [3] have reported examples of antiresonances in optical spectra of transition metal ions in crystals. The effect has been observed when a sharp absorption line is overlapped by a broad vibronic band. Recently Lempicki et al. [4] have reported absorption spectra of Cr^{+3} doped glasses exhibiting Fano antiresonances resulting from interaction of ^2E and $^2T_1$ states with a vibronically broadened $^4T_2$. In this letter we report preliminary results of fluorescence measurements on glasses doped with Cr^{+3} and Nd^{+3} ions. The features of the spectrum may be interpreted as antiresonances resulting from interaction of Nd^{+3} states ($^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$) with the vibrationally broadened $^4T_2$ state of Cr^{3+}, the origin of the $^4T_2 \rightarrow {}^4A_2$ fluorescence band, resembling the Fano antiresonance.

Experiment

The glass samples were kindly supplied by Jelenia Góra Optical Works. The composition of base glass was: P_2O_5 80.53%, Li_2O 11.16%, Al_2O_3 8.31%. The neodymium and chromium were added in the form of $Cr_2O - 0.50$ and $Nd_2O_3 - 1.00$. The samples were cut and polished into $2 \times 15 \times 20$ and $4 \times 4 \times 15$ mm. The absorption spectra were recorded on a Beckman 5240 spectrophotometer. The fluorescence was excited with an argon ion laser ILA 120 (Carl Zeiss Jena) tuned near 488 nm and recorded with a GDM 1000 monochromator (Carl Zeiss Jena) and an FD 29 photomultiplier (Carl Zeiss Jena).

Results

The absorption spectra of the samples doped with Cr^{+3}, Nd^{+3} and $Cr^{+3} + Nd^{+3}$ are shown in Figs. 1, 2, and 3, respectively.

The absorption band corresponding to the $^4A_2 \rightarrow {}^4T_2$ transition of Cr^{+3} is located at 500 – 800 nm. The two dips in the center of this band (Fig. 1, 3) were interpreted by Lempicki et al. [4] as Fano antiresonances resulting from intraconfigurational interaction of ^2E and $^2T_1$ states with a broadband $^4T_2$ state. The observed dips coincide almost exactly with the positions of ^2E and $^2T_1$ states. The difference between the real positions of the interacting states and the antiresonance dips observed is due to the coupling with the continuum. According to Lempicki this displace-

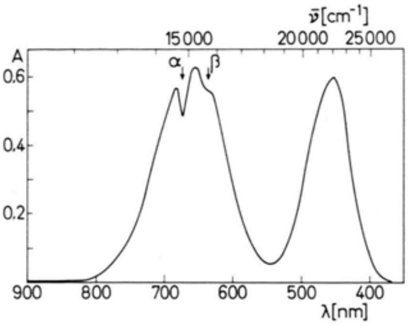

Fig. 1. Absorption spectrum of Cr^{+3} in glass at 300 K. The positions of Fano antiresonances are denoted by α and β.

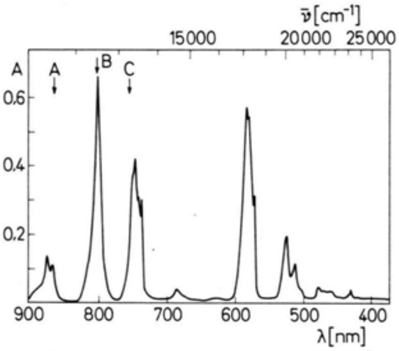

Fig. 2. Absorption spectrum of Nd^{+3} in glass. The positions of antiresonance dips are denoted by A, B, C.

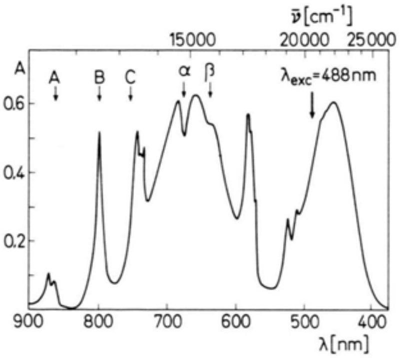

Fig. 3. Absorption spectrum of Cr^{+3} and Nd^{-3} doped glass. The positions of the Cr^{+3} Fano antiresonance dips are denoted by α and β.

Reprint requests to Dr. W. Stręk, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, 50-950 Wrocław/Polen

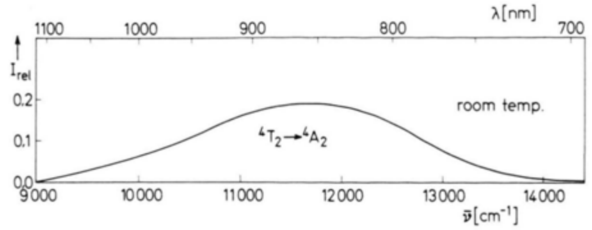

Fig. 4. Fluorescence spectra of Cr^{+3} in glass at 300 K.

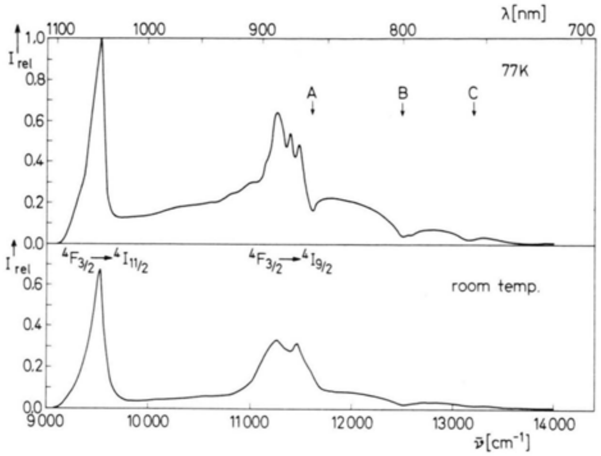

Fig. 5. Fluorescence spectra of Cr^{+3} and Nd^{+3} doped glass measured at 77 K and 300 K. The positions of antiresonance dips are denoted by A, B, C.

ment is a direct consequence of the inhomogeneous broadening of the $^4T_2$ band in glasses and is analogous to the Lamb shift.

The fluorescence of Cr^{+3} doped glass is shown in Figure 4. It originates from the $^4T_2$ level. Due to the large Stokes shift the fluorescence band is strongly vibrationally broadened.

The fluorescence of Nd^{+3} originates from the $^4F_{3/2}$ level. The peaks corresponding to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions are located at 11000 – 11700 cm^{-1} and 9000 – 9800 cm^{-1}, respectively. In the sample of mixed Cr and Nd the Nd fluorescence is overlapped by the Cr^{+3} fluorescence (see Figure 5). A comparison of the fluorescence spectra of the Cr^{+3} and $Cr^{+3} + Nd^{+3}$ doped glasses indicates the existence of characteristic antiresonance dips at 11600 cm^{-1} (A), 12500 cm^{-1} (B) and 13200 cm^{-1} (C). Their positions coincide well with the $^4F_{3/2}$, ($^4F_{5/2}$, $^2H_{9/2}$) and ($^4F_{7/2}$, $^4S_{3/2}$) absorption bands of Nd^{+3}, respectively. In Table 1 the positions of the dips and the energy levels of the Nd ion are listed.

Table 1. The correlation between the positions of antiresonance dips and absorption peaks of Nd^{+3}.

Dip position (cm^{-1})		Peak position of Nd^{+3} (cm^{-1})	
A.	11600	11467 11575	$^4F_{3/2}$
B.	12500 12570	12270 12500	($^4F_{5/2}$, $^2H_{9/2}$)
C.	13150	13400 13515 13605	($^4F_{7/2}$, $^4S_{3/2}$)

It is seen that the coincidence in case of the dip C is not satisfactory. Its position is slightly red shifted relative to the ($^4F_{7/2}$, $^4S_{3/2}$) band. The disrepancy between the position of the antiresonance dip and the respective absorption band is similar to the Fano antiresonance of the $^2T_1$ level in the absorption spectrum of Cr^{+3} in glass observed by Lempicki [4]. We identified this displacement with the Lamb shift. In case of the dips A and B the Lamb shifts are positive while for the dip C the Lamb shift is negative. The intensity of the antiresonance dips increases with decreasing temperature. For instance the dip A located at 11600 cm^{-1} coinciding with the higher Stark component of the $^4F_{3/2}$ level is observed markedly at 77 K and vanishes at 300 K. This is probably due to the Boltzmann population of the higher Stark components of the excited state which fluorescence at elevated temperature.

The antiresonance dips observed in the fluorescence spectrum of $Cr^{+3} + Nd^{+3}$ doped glass resemble the Fano antiresonances, however their origin is different. The theory of Fano antiresonances implies the assumption that the vibronically broadened band interacts intraconfigurationally with a discrete autoionized state of the same species. In our phenomenon the antiresonance dips result from interionic Cr-Nd interaction. It seems that between the overlap factor for the Cr-Nd energy transfer and the area of dips exists a close relation. The investigation of the dip area could give direct information about the overlap factor for the energy transfer.

The phenomenon of antiresonance dips in fluorescence spectra has not been reported previously. A theoretical examination of this effect is needed.

[1] U. Fano, Phys. Rev. **124,** 1866 (1966).
[2] U. Fano and J. W. Cooper, Phys. Rev. **A 137,** 1364 (1965).
[3] M. D. Sturge, H. J. Guggenheim, and M. H. L. Pryce, Phys. Rev. **B 2,** 2459 (1961).
[4] A. Lempicki, L. Andrews, C. J. Nettel, B. C. McCollum, and E. I. Solomon, Phys. Rev. Lett. **44,** 1234 (1980).