Spectroscopy of Cr^{3+} in Glasses: Fano Antiresonances and Vibronic "Lamb Shift"

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Absorption spectra of Cr^{3+}-doped glasses exhibit features which are interpreted as Fano antiresonances resulting from interaction of ^2E and $^2T_1$ states with a vibrationally broadened $^4T_2$. Inhomogeneous line broadening in glass permits the observation of a shift of sharp levels due to interaction with the quasicontinuum.

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We report preliminary conclusions reached from exhaustive investigation of octahedrally coordinated Cr^{3+} in phosphate, silicate, and borate glasses. Absorption spectra are interpreted in terms of an interaction between the sharp intra-t_2^3 levels ^2E and $^2T_1$, and the vibrationally broadened $^4T_2$ (t_2^2e) quasicontinuum, resulting in Fano-type antiresonances[1] similar to those first observed in $KMgF_3:V^{+2}$ by Sturge, Guggenheim, and Price.[2] This interpretation differs radically from previous work on similar materials, clears up controversial assignments of transitions,[3] and offers probably the most striking example of antiresonances in all solid state physics.

Spectroscopy of Cr^{3+} in glass is dominated by the low value of the ligand field parameter $10Dq$, ranging from 14 500 cm^{-1} in phosphates to 16 500 cm^{-1} in borates[4] (for ruby, $10Dq = 17\,000$ cm^{-1}). The low value of $10Dq$ places the $^4T_2$ level lowest resulting in broadband, Stokes-shifted fluorescence.

Figure 1 shows the long-wavelength $^4T_2 \leftarrow {}^4A_2$ absorption band for five different glasses. In all cases except curve *e*, a structure suggesting three subsidiary "peaks" is clearly seen. The interpretation of these "peaks" has been the subject of several controversial publications, the most recent by Brawer and White,[3] who also reviewed previous work. The source of the difficulty resides in simultaneously accounting for the overall width of the band and the shape and width of the three subbands. These difficulties are resolved if one views these features as resulting from Fano antiresonances.[1,5] This claim rests on the following considerations:

(1) From Fig. 1 it is clearly seen that it is the *center* (or valleys) of the features not the peaks, which are isoenergetic.

(2) As one progresses from low to high field (*a* to *e*), the main band moves towards shorter wavelength. As Dq/B increases, this is exactly what one would expect from the Tanabe-Sugano diagram[6] if the features were associated with the ^2E and $^2T_1$ states while the broad band represented the $^4T_2$ state. In the higher-field case of borates, we see that the features occur on the long-wavelength side of the band. Qualitatively similar effects have been found by Bates in sulfuric acid solutions.[7]

(3) Consider the "dip" at 14 800 cm^{-1} particularly in cuve *a* of Fig. 1. In no way can this be

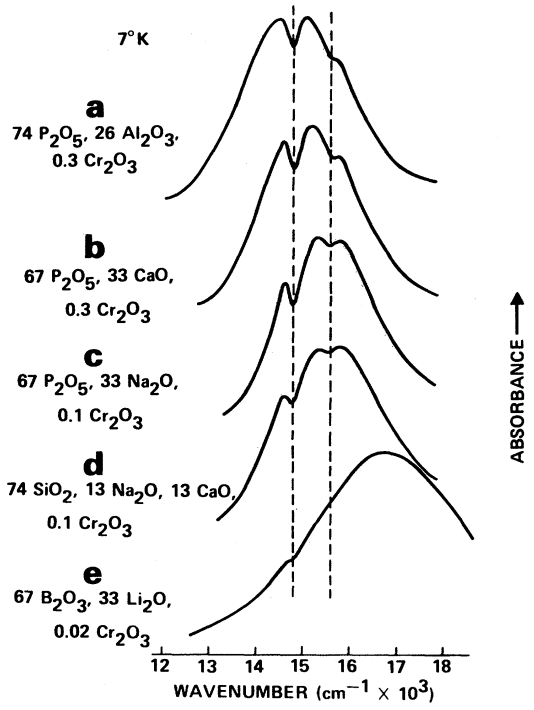

FIG. 1. Absorption spectra of Cr^{3+}-doped glasses at helium temperature (the room-temperature spectra are similar). The glass compositions are in mole percent.

the result of overlap of two displaced Gaussian bands given the asymmetry of the "peaks" on the right- and left-hand side of the dip. The "dip" is clearly a "notch" in *one* broad band and represents a *reduction* of absorption.

(4) In most glasses, in addition to the broad $^4T_2 \rightarrow {}^4A_2$ fluorescence, we observe a sharp emission line located between 14 550 and 14 660 cm^{-1}. This line has a characterisitc decay time of the order of a millisecond (roughly 20 times longer than that of the broad band) and a distinctly different excitation spectrum. We interpret this as the $^2E \rightarrow {}^4A_2$ emission (R line) originating from a small fraction of sites for which ^2E is the lowest excited state (high-field sites). This is supported by ample additional evidence for multiple sites and inhomogeneous broadening in all the glasses we have examined.[4] In general, the R line *does not* coincide with the low-energy "peak" [Fig. 2(a)] as has previously been assumed.

Based on these considerations we analyze the band shape in terms of the ratio $R(\omega)$ of the observed absorption profile to the background given by Fano theory (in the notation of Ref. 5):

$$R(\omega)=1+\sum_i \rho_i{}^2 \frac{q_i{}^2+2q_i\epsilon_i{}^{-1}}{1+\epsilon_i{}^2},$$

where

$$\epsilon_i=\frac{\omega-\omega_{ri}}{\gamma_i}, \quad q_i=\frac{\langle\Phi_i|z|\psi_0\rangle}{(\pi\gamma_i)^{1/2}\rho_i\langle\psi_{E,i}{}^d|z|\psi_0\rangle},$$

$$\gamma_i=\pi|\langle\psi_{E,i}{}^a|H_i|\varphi_i\rangle|^2, \quad \rho_i=\langle\psi_{E,i}{}^a|\psi_{E,i}{}^d\rangle.$$

The index i ranges over the number of sharp levels (2 in our case). This result holds if one neglects interactions between them via the continuum. φ_i is the wave function of the sharp level in absence of the interaction H_i with the continuum (spin-orbit in our case). Φ_i represents a modification of φ_i by the continuum and ψ_0 the ground state; z is the optical operator (electric or magnetic dipole). Following Ref. 5, the parameters $\rho_i{}^2 \leq 1$ are overlap integrals of $\psi_{E,i}{}^a$ and $\psi_{E,i}{}^d$ which arise, respectively, by autoionization of φ_i and by direct transition from ground state.

We select curve a of Fig. 1 for a presentation of the analysis. First a double Gaussian is chosen to fit the background absorption in the wings [Fig. 2(a)]. The ratio $R(\omega)$ is then obtained by use of the observed spectrum and the double Gaussian. This is shown as the continuous curve in Fig. 2(b). This curve is then decomposed into two antiresonance curves shown on Fig. 2(c). Their sum (less unity)[8] is then represented as the dotted curve in Fig. 2(b). The parameters ω_{ri}, q_i, ρi^2 and γ_i are listed on Fig. 2(c). The index $i=1$ corresponds to the ^2E state, and $i=2$ the $^2T_1$ state. A similar analysis has been performed for other curves of Fig. 1 with the exception of curve e. Data pertaining to the ^2E antiresonance are listed in Table I. We make the following comments concerning the results:

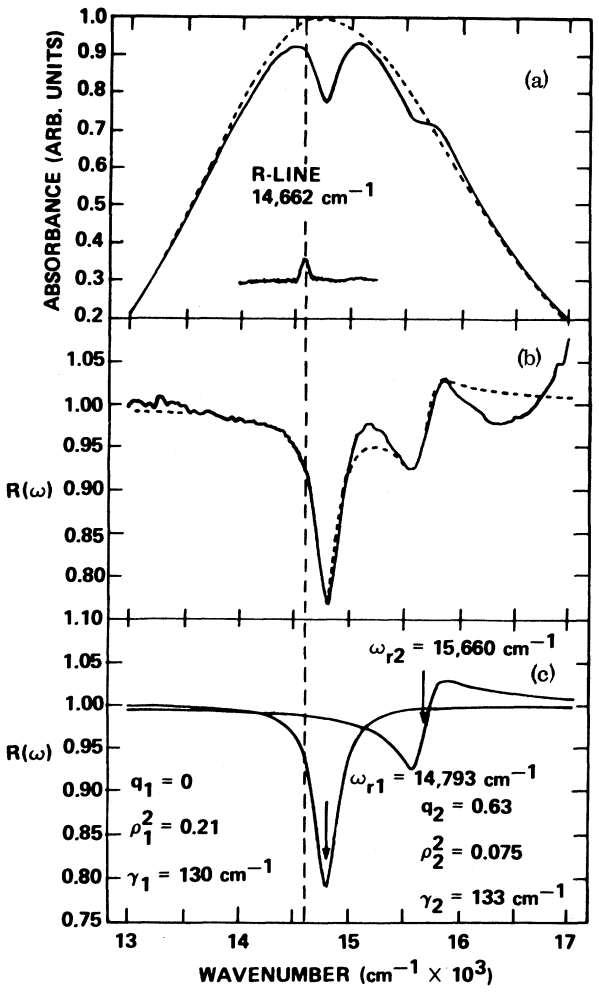

FIG. 2. (a) Continuous curve, repeat of curve a of Fig. 1; dashed curve, double Gaussian fit. Emission spectrum showing R line on the bottom. (b) Continuous curve, ratio $R(\omega)$ obtained from (a); dotted curve, fit of Eq. (1) to $R(\omega)$; (c) antiresonance curves for the two sharp states ^2E and $^2T_1$. Sum of these results are shown by the dotted curve in (b).

(1) Extraction of $R(\omega)$ depends critically on the choice of a background band shape. When the antiresonance effect is small, as in Ref. 2, the choice leaves little ambiguity. In the case of glass, the effect is much larger and correct

TABLE I. Parameters of ^2E antiresonance.

Glass	q_1	ρ_1^2	γ_1 (cm^{-1})	ω_{r1} (cm^{-1})	$\omega(R)$ (cm^{-1})	$\Delta\omega$ (cm^{-1})
Fig. 1, curve *a*	0	0.21	130	14793	14662	131
Fig. 1, curve *b*	0	0.25	150	14830	...[a]	168[b]
Fig. 1, curve *c*	−0.2	0.28	150	14800	14640	160
Fig. 1, curve *d*	−0.2	0.21	175	14780	14580	200

[a]Not observed.
[b]Assuming R-line position as in the glass shown in Fig. 1, curve *a*.

choice of an undistorted background is far more difficult. We consider the case in Fig. 2(a) where the ^2E antiresonance coincides almost exactly with the peak of the absorption curve as least subject to error from this source.

(2) Quality of samples (scattered light), contributions from the next higher absorption band ($^4T_1$), and the presence of some Cr^{6+} absorption render the fit in the $^2T_1$ region more uncertain. Therefore, we limit our discussion of the $^2T_1$ antiresonance to the data entered on Fig. 2(c).

(3) The departure of ρ^2 from unity signifies the existence of multiple continuua differently coupled to the sharp level.[1] In octahedral symmetry, not all of the spin-orbit components of $^4T_2$ mix with the components of ^2E and $^2T_1$. This fact has been recognized already in Ref. 2. Since depatures from O_h certainly certainly occur in glass, this mixing is more complete and therefore ρ^2 is larger than in a crystal.

(4) The difference $\Delta\omega = \omega_r - \omega$ (R line) represents the displacement of the ^2E level due to coupling with the continuum. This displacement, which is an analog of the Lamb shift, is given by[1]

$$\Delta\omega = \mathrm{P}\int \frac{|V|^2\rho(\omega)\,d\omega}{\omega(R)-\omega},$$

where V is the matrix element connecting the sharp level and the continuum, $\rho(\omega)$ is a density of states. The possibility of observing this shift is a direct consequence of the inhomogeneous broadening in glass and the ligand-field independence of the ^2E position. We believe that this is the first direct observation of such an effect in a solid. The numerical values of $\Delta\omega$ may be in doubt because they depend on details of the curve-fitting procedure which determines ω_r. Existence of $\Delta\omega$ and its positive value[9] is, however, assured, in view of the position of the R line relative to the ^2E antiresonance [Figs. 2(a) and 2(b)].

(5) As shown in Ref. 2, there exists an independent method of calculating q_i and γ_i from the Hilbert transform of the background absorption spectrum. We have performed such calculations and obtain for our most reliable case [Fig. 2(a)] $q_i = -0.03$ and $q_2 = 0.77$ in good agreement with observed values. Calculations of γ require the additional knowledge of the one electron spin-orbit coupling parameter[2] ξ' which is not available for glass. Inversely, calculating ξ' from the observed value of $\gamma_1 = 130\ cm^{-1}$ leads to $\xi' = 269\ cm^{-1}$. This has to be smaller than the face ion value of 292 cm^{-1} (Ref. 10) and is thus in the right direction. The actual value is probably still smaller because inhomogeneous broadening tends to increase the observed linewidth γ_1.

(6) Contributing to discrepancies are assumptions inherent in the basic theory such as uniform density of states and independence of q on energy. Clearly, the existence of the shift $\Delta\omega$ indicates that these assumptions are violated.

In conclusion, we feel that these results clear up the origins of the absorption features in Cr^{3+}-doped glass, illustrate the existence of a "Lamb shift" and suggest further extensions of the work.

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[8]For one sharp level, Eq. (1) takes the form $R = 1 + \rho^2 F(\epsilon)$. Curves on Fig. 2(c) are of this form. Adding contributions from two levels and maintaining the form of Eq. (1) requires subtraction of 1.

[9]$\Delta\omega > 0$ implies that $|V|^2 \rho(\omega)$ peaks below $\omega(R)$, i.e., for $\omega < \omega(R)$.

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Helium Synthesis, Neutrino Flavors, and Cosmological Implications

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The problem of the production of helium in the big bang is reexamined in the light of several recent astrophysical observations. These data, and theoretical particle-physics considerations, lead to some important inconsistencies in the standard big-bang model and suggest that a more complicated picture is needed. Thus, recent constraints on the number of neutrino flavors, as well as constraints on the mean density (openness) of the universe, need not be valid.

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It has recently been claimed that the "standard" big-bang scenerio for cosmological helium production imposes a stringent limit on the number of neutrino flavors.[1] Recent astronomical evidence and theoretical particle-physics considerations discussed here suggest, however, that inconsistencies of a serious nature may be present within the standard scenerio and that, until the cosmological questions have been resolved, it may be more useful to adhere to the conventional view that physics imposes constraints on cosmology rather than vice versa.

It is useful to assume that the observed helium abundance by weight Y in a source consists of universal "primordial" contribution Y_p and a contribution ΔY from ordinary stellar nucleosynthesis. Stellar evolution theory suggests that $\Delta Y > 0$ and that, furthermore, $\Delta Y \propto Z$, the abundance of heavier elements not made in the big bang. Thus $Y_p \leq \min\{Y_{\rm obs}\}$, the set of reliable observed astronomical helium abundances. Reported values of Y in our own and other galaxies range from 0.228 to 0.342, a 50% variation within star systems having undergone differing rates of stellar nucleosynthesis.[2-4] Studies of helium abundances in H II regions of blue compact and irregular galaxies yield lower values of Y because, as their large gas-to-total-mass ratios and small dust-to-gas ratios and Z values indicate, they have experienced less star production and stellar evolution. Of these systems, the most highly and reliably studied are the nearby Large and Small Magellanic Clouds (LMC, SMC).[2,5] Recent measurements of such galaxies, correlating ΔY with Z have suggested as value for $Y_p = 0.228 \pm 0.014$ (3 standard deviations). If the high-quality data from the Orion nebula (our own galaxy) and the LMC alone are used, a value $Y_p = 0.218$ is obtained.[2] If one takes account of the fact that abundances as low as 0.228 have been reported for three galaxies,[3,4] by taking for one of them, IIZw40, the reported[4] $Z = 0.0041$ and using the well-substantiated relation $\Delta Y \simeq 3Z$, a value for $Y_p = 0.216$ would be obtained. Thus, we consider the conservative value[4] $Y_p = 0.228$ to be an upper limit on Y_p (see Fig. 1).

Independent estimates of Y_p can be obtained from other astronomical quarters. Closer to home in our own galaxy, it should be noted that while the Orion region[4] has a value for Y of 0.280 ± 0.010, this region is young and has seen multiple generations of stellar nucleosynthesis. The oldest stars in our own galaxy have significantly lower Y values. Horizontal-branch stars in globular clusters are extremely poor in He, at least in their surface atmospheres[6] and, most recently, data from very old subdwarf stars[7] have indicated values of $Y = 0.19 \pm 0.02$. Models of nucleosynthesis in the Sun require a very low initial abundance of He and heavier elements in order to