

From the best fit of the paraexciton line shape a value for the chemical potential  $\mu$  of the gas can be obtained, which in turn allows one to determine a density of particles by calculating the expression  $\sum_K n_K = N$ , since it contains only fundamental constants and the mass of the particles. Taking  $m^* = 3m_0$  (Ref. 16) we obtain, for  $\mu/k_B T = -1.5$  at 19 K,  $N = 2.5 \times 10^{17} \text{ cm}^{-3}$ , a value one order of magnitude less than the critical density for Bose-Einstein condensation at the same  $T$ . It is instructive to compare this number with that obtained from the experimental conditions: Assuming an excited volume  $S\alpha^{-1} = 3 \times 10^{-7} \text{ cm}^3$ , where  $\alpha \sim 100 \text{ cm}^{-1}$  is the absorption coefficient at 595 nm, and taking  $\tau_p = 13 \text{ } \mu\text{sec}$  and an input power  $P \sim 30 \text{ mW}$ , one finds  $N \sim 4 \times 10^{18} \text{ cm}^{-3}$ . Clearly the neglect of exciton migration is not justified. This effect, together with local heating of the sample probably sets a limit to the chemical potential which can be reached with use of the present means of excitation.

In conclusion, we have shown the existence of excitons with very long lifetime in a direct-band-gap semiconductor. This material appears to be a good candidate for the observation of a Bose condensation of excitons.

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<sup>1</sup>See, for example, T. M. Rice, in *Lecture Notes in Physics*, edited by M. Ueta and Y. Nishina (Springer, Berlin, 1976), Vol. 57, p. 144.

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<sup>11</sup>The interpretation of the emission at 616.6 nm as being due to phonon-assisted paraexcitation recombination has been disputed by Petroff *et al.* (Ref. 9) because they could not detect the corresponding absorption edge. However, recently Bloch and Schwab (Ref. 6) measured this absorption using high sensitivity detection.

<sup>12</sup>It was not possible to measure it beyond  $T = 50 \text{ K}$ , because of the exponential increase of  $X_o - \Gamma_{15}^-$  in its vicinity.

<sup>13</sup>Solutions of the coupled rate equations neglecting exciton diffusion predict a two-exponential behavior for the paraexciton as well as for the orthoexciton if  $\gamma_t'$  is not negligible. The measured orthoexciton decay at 1.8 K ( $\gamma_t' = 0$ ), however, cannot be described in this framework, and shows the necessity of a more complex model.

<sup>14</sup>The longer orthoexciton lifetime at 2 K indicates that the ortho-para transfer rate is less efficient at this temperature.

<sup>15</sup>This difference in line shape seems to depend upon the irradiated part of the sample.

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## Optical Homogeneous Linewidths of $\text{Pr}^+$ in $\text{BeF}_2$ and $\text{GeO}_2$ Glasses

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Optical homogeneous linewidths of the  $^3F_0 - ^3H_4(1)$  transition of  $\text{Pr}^{3+}$  in  $\text{BeF}_2$  and  $\text{GeO}_2$  glasses reveal an anomalously smooth quadratic dependence on temperature from 8 to 300 K. The low-temperature behavior is consistent with a recent model of Lyo and Orbach involving an interaction with a single two-level system but the smooth quadratic behavior at all temperatures has deep consequences for the relative roles played by the ordinary phonons and the two-level system in line broadening.

Recently there has been some evidence that optical homogeneous linewidths of ions in glasses are anomalously broad at low temperatures in

comparison with those observed in crystalline hosts. Selzer and co-workers<sup>1</sup> reported results on the homogeneous linewidth of  $\text{Eu}^{3+}$  in a silicate

glass in the temperature range below 100 K and showed that the linewidth behaved almost quadratically with temperature in this range. Avouris, Compion, and El-Sayed<sup>2</sup> observed a  $T^2$  behavior for the linewidth of  $\text{Eu}^{3+}$  in a similar glass in the temperature range 200–300 K but there was no correlation between the two sets of results.

Whereas the high-temperature results are consistent with an ordinary two-phonon Raman broadening mechanism at temperatures near the Debye temperature, no such simple explanation was available for the low-temperature results. The purpose of this paper is to show that homogeneous linewidths of ions in glasses exhibit an anomalously smooth quadratic dependence on temperature at all temperatures in the range 6–300 K independent of the glass matrix. The behavior is shown to be consistent at low temperatures with a model developed recently by Lyo and Orbach<sup>3</sup> involving an interaction of the optically active ion with the disorder modes or two-level systems (TLS) which are known to exist in amorphous systems.

We choose  $\text{Pr}^{3+}$  as the optically active ion since its dynamical properties in crystalline hosts are very well characterized and understood.<sup>4,5</sup> The  ${}^3H_4(1)-{}^3P_0$  absorption line at low temperature in glasses has an inhomogeneous width of  $\sim 150 \text{ cm}^{-1}$  and a pulsed narrowband laser is used to selectively excite ions from within this inhomogeneous band. The line-narrowed fluorescence spectrum at early times after pulsed excitation reveals only one spectrally sharp feature, namely the resonant  ${}^3P_0-{}^3H_4(1)$  line. All of the other nonresonant transitions overlap as a result of large accidental degeneracies and possible vibronic sideband transitions. For a laser linewidth of 1 GHz the resonant line is homogeneously broadened in the temperature range of interest. We measure this width as a function of temperature at different excitation frequencies. Two different types of glasses are used,  $\text{BeF}_2$  and  $\text{GeO}_2$ . A 3-mole%  $\text{Pr}^{3+}$  concentration was used in both glasses. Time-resolved studies did not reveal any time evolution in the fluorescence spectrum at any temperature indicating that energy transfer is negligible in these systems. Details of the experimental apparatus are outlined elsewhere.<sup>6</sup>

The homogeneous width  $\Delta\nu_H$  was calculated from the observed linewidth in fluorescence with use of the approximation of Kushida and Takushi<sup>7</sup>

$$\Delta\nu_H = \frac{1}{2}\Delta\nu_m,$$

where  $\Delta\nu_m$  is the measured width after careful deconvolution of the instrumental width. The data

for the homogeneous linewidth in  $\text{BeF}_2$  and  $\text{GeO}_2$  are presented in Fig. 1 as a function of temperature in the form of a log-log plot. A simple power dependence on  $T$  is evident over the whole temperature range for both glasses:

$$\Delta\nu_H \propto T^{1.85 \pm 0.2} \text{ (for } \text{BeF}_2\text{),}$$

$$\Delta\nu_H \propto T^{1.88 \pm 0.2} \text{ (for } \text{GeO}_2\text{).}$$

For comparison Fig. 1 also includes data on the homogeneous linewidth for the same transition of  $\text{Pr}^{3+}$  in the crystalline host  $\text{LaF}_3:\text{Pr}^{3+}$ , obtained from Refs. 4 and 5. In the high-temperature range the crystalline linewidths are comparable to those in the glasses and follow the same pattern with temperature. As the temperature is lowered below 100 K the crystalline linewidth deviates considerably from that in the glasses, becoming very small at low  $T$ . The order-of-magnitude difference in the linewidths at low  $T$  reveals the anomalous aspect of the glasses and is consistent with previous findings.<sup>1</sup>

To see this anomaly more clearly we note that the linewidth of the  ${}^3P_0-{}^3H_4(1)$  transition of Pr in  $\text{LaF}_3$  is well understood in terms of two-phonon Raman and one-phonon direct broadening mech-

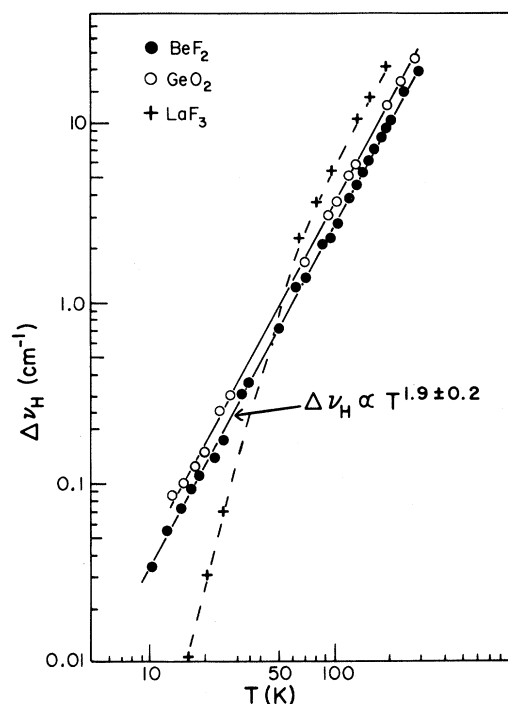


FIG. 1. Log-log plot of the temperature dependence of the  ${}^3P_0-{}^3H_4(1)$  homogeneous linewidth of  $\text{Pr}^{3+}$  in  $\text{BeF}_2$  and  $\text{GeO}_2$  glasses and in  $\text{LaF}_3$  crystal.

anisms.<sup>4,5</sup> The Raman process approaches a  $T^2$  behavior for  $T \geq 0.5T_D$ , where  $T_D$ , the Debye temperature, is 350 K in  $\text{LaF}_3$ . At lower temperatures the Raman contribution to the linewidth drops off rapidly at  $T^7$ , and a one-phonon direct process in the ground state becomes dominant.

The similarity of the linewidth behavior in the glass and in the crystalline host at high temperatures suggests that the same mechanism is responsible for the broadening in both glasses and crystalline systems, the Raman mechanism. This is to be expected since the Debye temperatures<sup>8</sup> of  $\text{BeF}_2$  and  $\text{GeO}_2$  are 380 and 308 K, respectively, similar to the Debye temperature of  $\text{LaF}_3$ . The smooth continuation of the  $T^2$  behavior down to the lowest temperature in the glasses, however, would suggest that the high-temperature Raman process is dominant at low temperatures also. Such a  $T^2$  Raman process operating as low as 10 K would entail an effective Debye temperature of  $\approx 50$  K. Since the Raman broadening mechanism is strongly dependent on the extent of the local strain introduced in the neighborhood of the Pr ion by the phonons, it is important to consider the nature of the low-energy phonons in glasses. Because of the amorphous nature of glasses it has been suggested<sup>9</sup> that the phonons are more localized in glasses than in the more ordered crystalline solids. If there is a high density of low-energy phonon modes and if they are sufficiently localized, then the large strains introduced in the neighborhood of the  $\text{Pr}^{3+}$  ion may make them more important in line broadening than the higher-energy optical modes. This could give effectively a low Debye temperature. Normalized Raman-scattering spectra from glasses<sup>10</sup> together with theoretical calculations on the spatial extent of the phonons<sup>9</sup> indicates that the modes are spatially very delocalized on the scale of the amorphous "lattice." It is unlikely then that these phonons would contribute significantly to the Raman broadening process at low temperatures. This does not rule out the possibility, however, that localized modes exist in glasses in association with the Pr ion such as, for example, the TLS which are either not Raman active or else have a very low density of states and which are responsible for the observed broadening.

A second possible cause for the anomalous broadening at low temperatures in glasses is that there is an inhomogeneous contribution to the linewidth which only becomes evident at low temperatures. Such might be the case if some of the ligands surrounding the Pr ion could exist in

more than one equilibrium configuration qualitatively similar to the TLS model for an array of atoms in a glass.<sup>11</sup> If in the course of a measurement time ( $\approx 6 \mu\text{s}$ ) the ligands tunnel back and forth slowly enough so as not to contribute to the dephasing time of the mutually excited ions, then the energy levels would change giving rise to an inhomogeneous broadening of the transitions. Such an inhomogeneous contribution would be reflected in a Gaussian line shape. A careful fit to the observed lines, however, shows that they are truly Lorentzian in shape and hence are homogeneously broadened.

We cannot totally discount the possibility that the large accidental degeneracies possible in amorphous systems are not partially responsible for the anomalous linewidth. Pr ions in very different environments can accidentally have the same  $^3P_0$ - $^3H_4(1)$  splitting but with different homogeneous linewidths. Since we can excite all of these ions with the laser, the measured linewidth would be some weighted convolution of the individual widths and so misleadingly broad. The linewidth varies by only a factor of 2, however, across the inhomogeneous line (Fig. 2) and this is insufficient to account for the observed widths at low temperatures.

As mentioned previously localized low-energy modes not observed directly in scattering experiments can contribute strongly to the broadening of optical transitions. It has now been established that amorphous systems do possess such modes called TLS which have been interpreted as sites of double-well potentials across which tunneling of the glass atoms or groups of atoms can occur. These modes give rise to anomalies in most properties of amorphous materials at very low temperature<sup>12</sup> and their existence has clearly been established in saturable ultrasonic attenuation experiments.<sup>13</sup> The density of states of these modes for low energies is believed to be constant but very low by comparison with that of the ordinary phonons. A large uncertainty exists, however, as to the nature and density of higher-energy modes. The very localized nature of the modes can give a large contribution to linewidths of neighboring optically active ions despite their low density of states. Selzer and co-workers<sup>1</sup> considered the interaction between pairs of these TLS as a broadening mechanism but a linear dependence on  $T$  was predicted in disagreement with the experimental results. More recently Lyo and Orbach<sup>3</sup> have treated the interaction between the optical ion and a single TLS with a simultane-

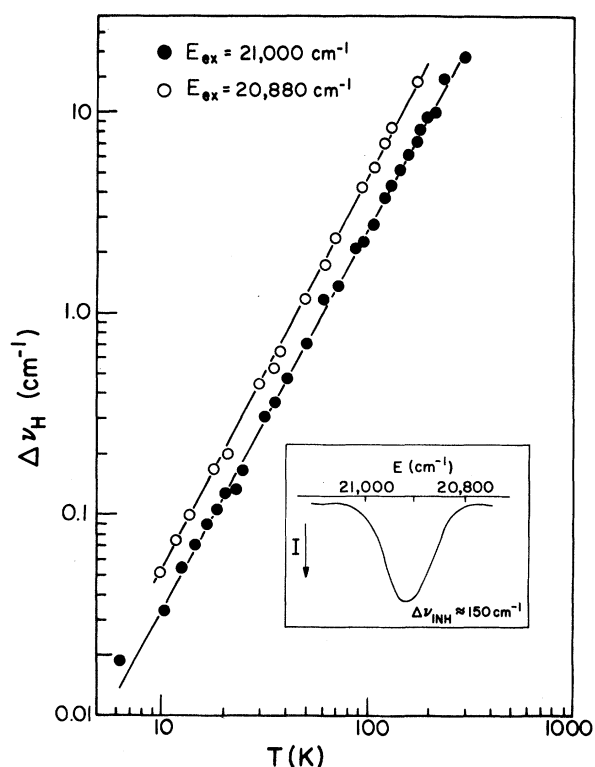


FIG. 2. Log-log plot of the  ${}^3P_0$ - ${}^3H_4(1)$  homogeneous linewidth of  $\text{Pr}^{3+}$  in  $\text{BeF}_2$  as a function of temperature for two different excitation frequencies in the inhomogeneous line. The inhomogeneous absorption profile for this transition is shown in the inset.

ous modulation at the TLS site by a phonon. By an explicit energy dependence in the perturbation process and using estimated values of Anderson, Halperin, and Varma for the TLS density of states and known parameters of  $\text{BeF}_2$  the temperature dependence of the homogeneous linewidth for  $T < T_D$  is calculated to be

$$\Delta\nu_H = 1.45\langle V^2 \rangle 10^{-8} T^2 \text{ cm}^{-1},$$

where  $\langle V^2 \rangle$  denotes an average value of  $V^2$ , and  $V$  is the difference in interaction energy of the TLS with the Pr ion in the excited and ground states. For  $T \geq T_D$  a linear dependence on  $T$  is calculated. The predicted  $T^2$  behavior at low temperatures is in agreement with the behavior observed in Fig. 1 for both types of glasses. Calculating actual numerical values for the linewidth depends strongly on the unknown quantity  $\langle V^2 \rangle$ . Lyo and Orbach assigned to this quantity an upper limit which is the inhomogeneous width of the  ${}^3P_0$ - ${}^3H_4(1)$  transition, measured to be  $150 \text{ cm}^{-1}$ . The actual value may be much smaller than  $150 \text{ cm}^{-1}$  but using this assumption a homogeneous line-

width of  $0.03 \text{ cm}^{-1}$  at 10 K is calculated, in reasonable agreement with our experimental results.

An important feature of the curves in Fig. 1 is the fact that the data follow a simple  $T^2$  behavior over the whole temperature range 8–300 K. As noted earlier, a Raman-type broadening is expected to predominate at the high-temperature region. If the low-temperature broadening is indeed due to the TLS, we would expect to see a break in the slope on going from low temperature to high temperature. Since the broadening mechanisms are expected to depend differently on the position in the inhomogeneous line, the break should manifest itself as a change in the ratio of the linewidths at two different frequencies on going from low temperature to high temperature. We have measured the homogeneous linewidth as a function of excitation frequency and temperature in the  $\text{BeF}_2$  glass and the data are presented in Fig. 2 for two extreme points,  $120 \text{ cm}^{-1}$  apart, in the inhomogeneous line which is shown as an inset in Fig. 2. Within experimental error no break in the slope is observed at any frequency and the ratio between the two curves is constant with a value of  $\approx 2$  at all temperatures.

An implicit assumption in the calculations of Lyo and Orbach concerns the TLS density of states which is taken to be almost constant. The density of states of high-energy TLS modes is not known, however, and may decrease rapidly above a certain energy. This would be reflected in a decrease in the TLS contribution to the linewidth above some temperature. This, coupled to the fact that the high-temperature TLS broadening tends toward a linear dependence on  $T$ , may mean a smooth changeover from the low-temperature TLS regime to the high-temperature Raman regime without any noticeable deviation. Conversely, it is possible that the TLS broadening mechanism dominates at all temperatures in the region 10–300 K. It is interesting in this regard to note that in the nuclear spin-lattice relaxation measurements of Szeftel and Alloul<sup>14</sup> and of Rubinstein *et al.*<sup>15</sup> the ordinary Raman process was not evident at temperatures even as high as 100 K. Clearly, a theoretical treatment of the high-energy TLS is necessary to calculate their density of states.

In summary, we have shown that the anomalous homogeneous linewidths of optical transitions in glass are a general feature of amorphous systems and are well correlated with an interaction with the TLS. The lack of distinction between the low-temperature and high-temperature broaden-

ing process shows that a deeper investigation of the high-energy TLS and any other anomalous amorphous modes and their distinction, if any, from normal phonon modes of comparable energy is necessary before a full understanding is reached.

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## Heats of Formation of Transition-Metal Alloys

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This Letter proposes a scheme for obtaining the  $d$ -electron energy-band parameters to be used in a simple analytic model of the alloy heat of formation,  $\Delta H$ . The scheme employs, as an intermediate step, the equalization of the local chemical potentials of the two sites. Calculations for  $3d$ ,  $4d$ , and  $5d$  metal alloys yield  $\Delta H$  in accord with experimental trends, but, unlike earlier estimates, with  $d$  charge transfer in the direction indicated by experiment.

Predictions of heats of formation of alloys,  $\Delta H$ , have been the object of considerable recent attention. Semiempirical schemes employing model parameters as well as electron energy band approaches have been used with semiquantitative success.

Miedema and associates employed<sup>1</sup> a cellular model for the heat of formation, which for transition metals has the form

$$\Delta H \propto [-P(\Delta\phi)^2 + Q(\Delta n^{1/3})^2]. \quad (1)$$

The first term, involving difference in electronegativities,  $\phi$ , of the constituent atoms, is negative and generally dominates, while the second, associated with mismatch in the electron densities,  $n$ , at the surfaces of the atomic Wigner-Seitz cells, is a competing positive term. Starting with work-function and bulk-modulus data, Miedema was able to adjust the  $\phi$  and  $n$  so that the known signs of  $\Delta H$  were reproduced. In a complementary effort, Alonso and Girifalco performed<sup>2</sup> cellular calculations exploring the con-