

Two-Level Systems and Excited-State Transitions in Fluorite Mixed Crystals and Silica Glass

S. A. FitzGerald,¹ J. A. Campbell,² and A. J. Sievers¹

¹Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

²Department of Physics, University of Canterbury, Christchurch, New Zealand

(Received 14 July 1994)

Low-temperature far-infrared absorption measurements have been made on a number of alkaline earth:lanthanum fluoride mixed crystals with the fluorite structure. In the mm wave region a continuous distribution of two-level glassy states is identified as being very similar to that previously found for glasses. At shorter wavelengths a characteristic temperature dependence associated with excited state transitions is observed in these mixed crystals. When silica glass is examined with the same precision, similar excited state transitions are found.

PACS numbers: 63.50.+x, 61.43.Fs, 78.30.Ly

Low-temperature specific heat measurements on glasses reveal a linear temperature dependence [1] quite different from that found for crystals. The introduction of two-level systems (TLS's) [2,3] in which the low lying dynamics of amorphous materials is characterized by atoms or groups of atoms tunneling has enjoyed outstanding success in explaining this and other observations. Although these materials have been studied for over 20 years with a variety of experimental techniques and theoretical models [4–8], the source of the TLS's described in these original proposals remains a mystery. For example, a characteristic property of tunneling systems is that they have excited states [9], but these have never been identified in amorphous materials. A number of far-infrared (ir) measurements have shown that the absorption over most of the vibrational region of glasses is large and temperature independent [10–12], but two studies demonstrated the presence of a temperature dependent TLS in glasses throughout the millimeter wave region [13,14]. From a systematic study of a large number of glasses, Bösch [14] concluded that the temperature dependent mm wave properties of glasses could be described by a superposition of three processes: at the lowest temperatures by resonant absorption of a uniform distribution of TLS, at higher temperatures by phonon assisted tunneling, and by thermally activated relaxation effects. The first observation [15] that TLS could be produced in dielectric crystals without a molecular component was made with refractory yttria-stabilized zirconia. The second observation [16] came from microwave measurements on $(MF_2)_{1-x}:(RF_3)_x$, where $M = \text{Ca, Sr, Ba}$; $R = \text{Lu, Y}$ up to $x = 0.3$. Thermal measurements [17] on the related mixed crystal $(\text{BaF}_2)_{1-x}:(\text{LaF}_3)_x$ confirmed that a continuous distribution of TLS does occur at low frequencies and that its number density depends on x between $x = 0.045$ and 0.33.

In this Letter far-ir results are described which show a continuous distribution of TLS's in fifteen different alkaline earth fluoride:lanthanum fluoride (AEF:LF) mixed crystals with the fluorite structure, some of which, $(\text{CaF}_2)_{1-x}:(\text{LaF}_3)_x$ and $(\text{BaF}_2)_{1-x}:(\text{LaF}_3)_x$, with $x = 0.05$

to 0.35, are considered here in some detail. The transparency of these crystals at higher frequencies permits us to identify temperature dependent TLS excited state transitions for both systems. Because of the remarkably universal character of these temperature and frequency dependent results, silica glass is then investigated with precise higher frequency measurements. Similar excited state transitions for TLS's are found whose transition frequencies coincide with the thermal conductivity plateau previously identified in the thermal properties of glasses [4].

Low-temperature far-ir measurements have been carried out on mixed AEF:LF crystals and soda-lime-silica glass, using a lamellar grating interferometer at frequencies between $3\text{--}25\text{ cm}^{-1}$ in conjunction with a 0.3 K ^3He -cooled bolometer and using a commercial fast scanning Michelson interferometer with a 1.6 K composite Si bolometer for frequencies between $15\text{--}50\text{ cm}^{-1}$. Sample temperature is determined by means of a calibrated Allen Bradley carbon resistor. The doped AEF:LF 10 mm diameter boules are grown from the melt under vacuum in a graphite crucible using the Stockbarger technique. Representative samples are analyzed by x-ray diffraction, to insure that they are single crystals. The lanthanum concentration, checked by x-ray fluorescence measurements, typically show a 10%–15% gradient in concentration along a 5 cm boule. The glass samples, of soda lime-silica, (72 wt % SiO_2 , 17 wt % Na_2O , 9 wt % CaO , ~ 2 wt % traces) consist of 10 mm diameter disks cut from 1.5 mm thick microscope slides.

Mixed crystals of $(MF_2)_{1-x}:(\text{LaF}_3)_x$, where $M = \text{Ca}^{2+}$, Sr^{2+} , or Ba^{2+} have been measured in the far-ir spectral region. For each crystal, the absorption first decreases at the lowest frequencies with increasing temperature from 1.4 to ~ 10 K, indicating the presence of a two-level spectrum and then grows as the temperature is increased further. The magnitude of the TLS spectrum observed in each host first grows linearly as a function of x and then saturates and remains constant at larger concentrations. This saturation value is observed to depend on the host cation size, ranging from a low value $x \approx 0.05$ for CaF_2

through $x \approx 0.2$ for SrF_2 and increasing to a concentration of $x \approx 0.35$ for BaF_2 . The temperature dependence of typical characteristic spectral features for some of the hosts are presented below.

Figure 1 shows the temperature dependent absorption spectrum of $(\text{CaF}_2)_{0.8}:(\text{LaF}_3)_{0.2}$ over the far-ir spectral region. At low frequencies, the largest absorption occurs at the lowest temperatures. With increasing temperature, the magnitude of the absorption coefficient decreases, reaching a minimum at about 15 K and then increases again at higher temperatures. For frequencies above 20 cm^{-1} , the relative change in the absorption coefficient with temperature is quite small.

The analysis of typical TLS data is shown in Fig. 2. Here temperature dependent far-ir data for $(\text{BaF}_2)_{0.9}:(\text{LaF}_3)_{0.1}$ are shown. The temperature dependent results at each frequency are extracted from a series of absorption spectra taken at discrete temperatures ranging from 1.4 to 10 K with the frequency ranging from 3 to 9 cm^{-1} . Subtraction of the absorption coefficient at two different temperatures removes the temperature independent contribution to the spectrum. If two-level resonant absorption is dominant, then [6]

$$\Delta\alpha(T; T_R) = \alpha(T) - \alpha(T_R) = -\omega G(\omega)\Delta P(T, T), \quad (1)$$

where $G(\omega) \equiv 4\pi^2 n_e(\omega)\mu^2/\sqrt{\epsilon}c$ and $\Delta P(T, T_R) \equiv [\tanh(\hbar\omega/2kT_R) - \tanh(\hbar\omega/2kT)]$. Here $n_e(\omega)$ is the density of states of TLS coupling to the electric field, μ is the transition matrix element of the TLS without local field correction, c is the speed of light in vacuum, ϵ is the dc dielectric constant, and the $\tanh(\hbar\omega/2kT)$ reflects the thermal population difference between the two levels at temperature T . The solid curves given in Fig. 2 are the predicted response from Eq. (1) with the reference temperature $T_R = 1.4 \text{ K}$. The origin for each frequency

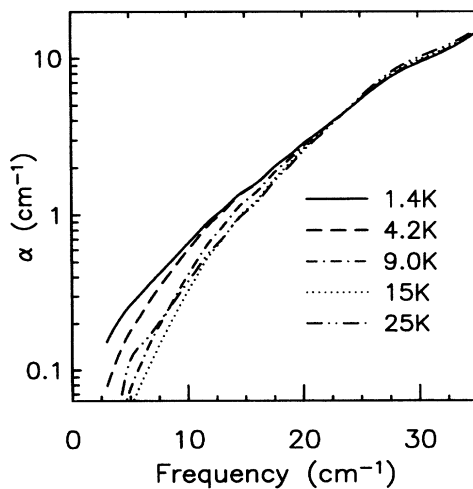


FIG. 1. Frequency and temperature dependence of the absorption coefficient for a $(\text{CaF}_2)_{0.8}:(\text{LaF}_3)_{0.2}$ fluorite mixed crystal. The resolution is 1.5 cm^{-1} .

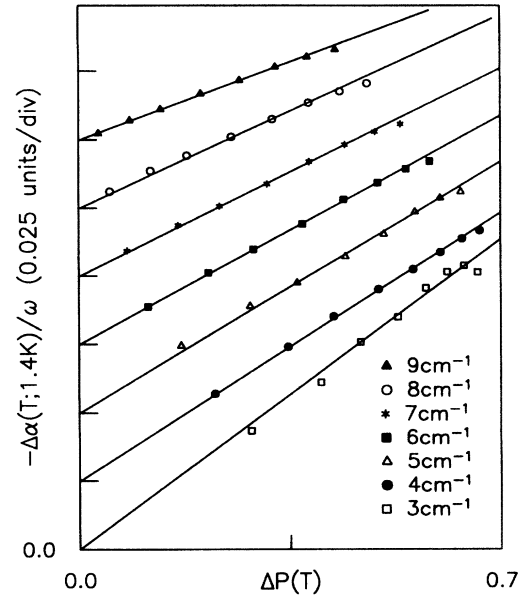


FIG. 2. Comparison of theory and experiment for the thermal population difference of two-level systems in $(\text{BaF}_2)_{0.9}:(\text{LaF}_3)_{0.1}$. See Eq. (1) in the text for definitions. $T_R = 1.4 \text{ K}$. Spectra were taken at eight other temperatures of 3.2, 4.2, 5.0, 6.0, 7.0, 8.0, 9.0, and 10 K. Data are shown for seven frequencies between 3 and 9 cm^{-1} . In each case the origin has been displaced for clarity and each line represents the best linear fit which passes through the origin.

curve has been displaced for clarity. If the resonant TLS process dominates then with no adjustable parameters, the data must follow straight lines. The actual slope of each straight line gives $G(\omega)$.

The good agreement between theory and experiment presented in Fig. 2 is typical for the AEF:LF crystals and only at the highest temperatures and frequencies are deviations from linear dependence found. The data at 3 cm^{-1} identify the lower frequency limit of our measurement technique. Here the small source intensity and reduced size of the temperature dependent effect produces significant errors. The value and frequency dependence of $G(\omega)$ depend on the particular host lattice, but in every case a broad, smooth distribution is observed. From data such as Fig. 2 we conclude that the low temperature mm wave absorption from 3 to 9 cm^{-1} in AEF:LF mixed crystals is dominated by the resonance absorption resulting from a distribution of TLS.

Having established that the absorptive properties of these mixed crystals behave like a glass below 10 cm^{-1} , we next examine data at higher frequencies and temperatures. Figure 3 shows $\Delta\alpha(T; 1.4 \text{ K})$ for $(\text{CaF}_2)_{0.8}:(\text{LaF}_3)_{0.2}$ up to 50 K. For frequencies below 22 cm^{-1} the absorption coefficient initially decreases with increasing temperature as described above but by 50 K, a dramatic increase in absorption occurs at all frequencies. This is the thermal activation of relaxation absorption pro-

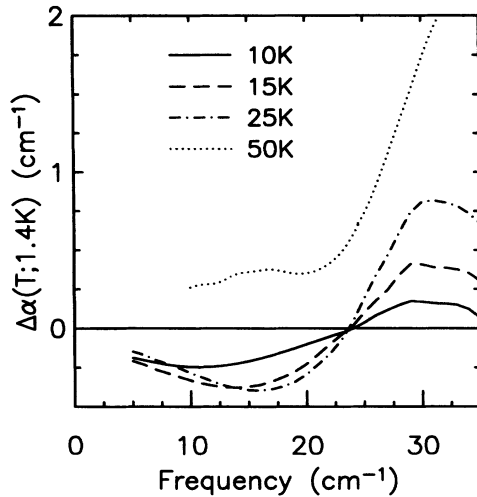


FIG. 3. The temperature-induced change in the absorption coefficient for $(\text{CaF}_2)_{0.8}:(\text{LaF}_3)_{0.2}$ versus frequency. Note that at temperatures below 25 K all curves cross near the same frequency. At higher temperatures, relaxation absorption processes become important. See the dotted curve. The resolution is 1.5 cm^{-1} .

cesses and not difference band absorption involving crystal phonon modes [18], since a similar temperature dependence is not observed for low concentration samples. We restrict our discussion to data taken at temperatures of 15 K or lower so that these high temperature thermal processes are quenched. Notice that all the low temperature $\Delta\alpha(T; 1.4 \text{ K})$ data in Fig. 3 come together near 22 cm^{-1} ; in addition, the $\Delta\alpha$ curves peak at about 31 cm^{-1} and then decrease again with increasing frequency. The crossing frequency is surprisingly constant and shifts by no more than 5% to 15%, with temperature depending on the host cation. In addition, the frequency where $\Delta\alpha(10 \text{ K}; 1.4 \text{ K})$ goes to zero is relatively independent of the lanthanum fluoride concentration, varying by less than 10% over the complete concentration range studied, but the host cation does influence the crossing frequency which is 22 cm^{-1} for CaF_2 , 16 cm^{-1} for SrF_2 , and 13.5 cm^{-1} for BaF_2 .

Figure 4(a) shows the $\Delta\alpha(T; 4.2 \text{ K})$ for $(\text{BaF}_2)_{0.77}:(\text{LaF}_3)_{0.23}$ and $(\text{CaF}_2)_{0.87}:(\text{LaF}_3)_{0.13}$ over the entire frequency interval that we have examined. Because of the small zero crossing frequencies of the mixed BaF_2 host, see curves (i), we have been able to examine its excited state properties over the largest relative frequency interval. We find two additional zero crossings near 27 and 43 cm^{-1} . At the highest frequencies, the relative size of the temperature-induced effect becomes too small to measure, even though on the $\Delta\alpha$ scale in Fig. 4(a), the magnitude of the peak in each frequency interval is comparable. Similar results are found for the CaF_2 host; see solid and dashed curves (ii) in Fig. 4(a). Because of the larger characteristic frequency of the first zero crossing

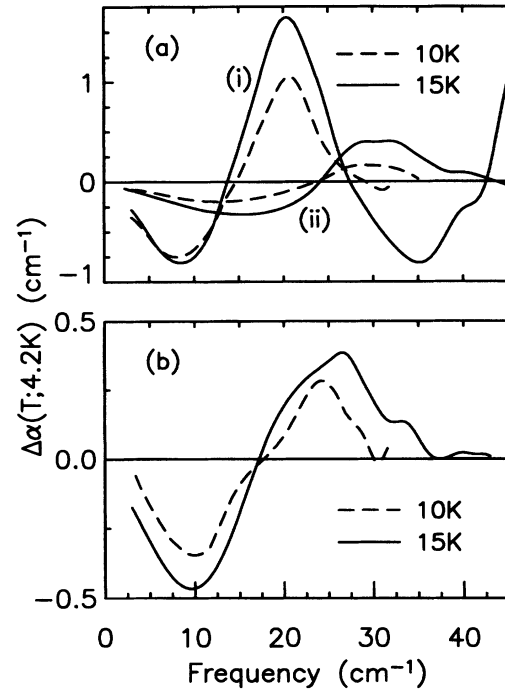


FIG. 4. The temperature-induced changes in the absorption coefficient versus frequency in fluorite mixed crystals and silica glass over an extended interval. For each sample are shown $\Delta\alpha(10 \text{ K}; 4.2 \text{ K})$ (dashed) and $\Delta\alpha(15 \text{ K}; 4.2 \text{ K})$ (solid). (a) $(\text{BaF}_2)_{0.77}:(\text{LaF}_3)_{0.23}$ curves (i); $(\text{CaF}_2)_{0.87}:(\text{LaF}_3)_{0.13}$ curves (ii). (b) Soda-lime-silica glass. Note that the zero crossing at 17 cm^{-1} is nearly independent of temperature just as for the mixed crystal data shown in Figs. 3 and 4(a).

only one additional crossing near 43 cm^{-1} is identified in $\Delta\alpha(15; 4.2 \text{ K})$ before this crystal becomes opaque.

We now show that these zero crossing frequencies cannot be explained by the processes that have been used previously with TLS in glasses. In principle, besides resonant TLS absorption, additional temperature dependent absorption due to phonon-assisted tunneling could occur. It would have the form [19]

$$\alpha \propto \int_0^\infty dE n_e(E) \frac{df(E)}{dE} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (2)$$

where $f = [1 + \exp(E/kT)]^{-1}$ and τ the relaxation time is given by $\tau = K^{-1} \tanh(E/2kT)/E^3$, where K is a constant. A second mechanism which also has the Debye relaxation form given by Eq. (2) can occur via temperature-activated relaxation over the potential barrier between levels with a relaxation time of the form $\tau = \tau_0 \exp(V/kT)$. Since both of these processes produce increasing absorption with increasing temperature, they could give rise to the first zero crossing observed in the data, but the crossing frequency would then be strongly temperature dependent. This is not seen, e.g., Fig. 3. In order for this zero crossing to remain fixed within the framework of this model, the density of the two level

spectrum should terminate near this crossing frequency. However, the relaxation effects described by Eq. (2) cannot produce additional zero crossing at still larger frequencies of the type shown in Fig. 4(a), a key feature of our data.

We propose that these higher frequency features in Fig. 4(a) are associated with excited states of the TLS. The change in sign of $\Delta\alpha$ at higher frequencies is a natural consequence of the oscillator strength sum rule which states that $\int \alpha(\omega, T) d\omega = \text{const}$ [20]. With increasing temperature, the absorption coefficient for the tunneling transitions decreases, but at the same time because of the oscillator strength sum rule, the absorption coefficient for the TLS excited state transitions must increase by a corresponding amount. One surprising result is that although the strength of the TLS spectrum depends on the LaF_3 concentration x , the frequency spectrum does not, since the zero crossing frequency in Fig. 3, in particular, and for all the AEF:LF crystals, in general, is essentially independent of both ΔT and x .

To determine whether this temperature-induced spectroscopic signature is a specialized feature of AEF:LF mixed crystals or a more general property of TLS, we have also investigated, with increased precision, the corresponding far-ir properties of a silicate glass. We chose soda-lime-silica glass, one of the strongest far-ir absorbers [14]. Figure 4(b) shows $\Delta\alpha(10 \text{ K}; 4.2 \text{ K})$ and $\Delta\alpha(15 \text{ K}; 4.2 \text{ K})$, respectively [21]. For both 10 and 15 K, $\Delta\alpha$ is initially negative, crosses zero at approximately 17 cm^{-1} , becomes positive in an intermediate frequency region, and then returns to zero at ≈ 30 and 37 cm^{-1} , respectively, where the glass becomes opaque even at 0.1 mm thickness. In each case, the positive and negative areas are roughly equal, as expected if both contributions stem from resonant transitions within the TLS manifold. As was found in the mixed crystal work, the zero crossings occur at roughly equal frequency intervals so that Figs. 4(a) and 4(b) display qualitatively similar s-shaped curves. It is worth noting that these excited states of the TLS's for the soda-lime-silica glass occur in the same frequency interval as the corresponding thermal conductivity plateau [1].

In summary, we have demonstrated that a continuous distribution of TLS's occurs in the mm wave spectrum of AEF:LF fluorite mixed crystals, by showing that the temperature dependent results are similar to those previously found for TLS in glasses. Studies of these mixed crystals at higher frequencies resolve new spectral features that are not a consequence of relaxation effects but instead correspond to excited state transitions of the TLS. The characteristic temperature dependent features

are extremely robust from concentration to concentration and host to host crystal. Finally, a similar temperature-induced excited-state signature has been identified in a silicate glass with an energy scale that provides a natural explanation of the universal thermal conductivity plateau found in all glasses [7].

Helpful discussions with R. O. Pohl, J. P. Sethna, and R. H. Silsbee are gratefully acknowledged. We would also like to thank J. Hunt, N. Andrews, and M. Rich for technical assistance in sample characterization and B. Plapp for constructing an optical insert. This work is supported by NSF-DMR-9312381, NSF-INT-8922841, ARO-DAAL03-92-G-0369, and at Canterbury by the New Zealand Universities Grants Committee. In addition, this research made use of the Materials Research Laboratory facilities supported by the National Science Foundation under Grant No. DMR-9121654.

-
- [1] R. C. Zeller and R. O. Pohl, *Phys. Rev. B* **4**, 2029 (1971).
 - [2] P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972).
 - [3] W. A. Phillips, *J. Low Temp. Phys.* **7**, 351 (1972).
 - [4] W. A. Phillips, in *Amorphous Solids*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).
 - [5] S. Hunkliger and A. K. Raychaudhuri, *Prog. Low Temp. Phys.* **9**, 265 (1986).
 - [6] W. A. Phillips, *Rep. Prog. Phys.* **50**, 1657 (1987).
 - [7] C. C. Yu and A. J. Leggett, *Comments Condens. Matter Phys.* **14**, 231 (1988).
 - [8] D. J. Salvino *et al.*, *Phys. Rev. Lett.* **73**, 268 (1994).
 - [9] R. D. Kirby, A. E. Hughes, and A. J. Sievers, *Phys. Rev. B* **2**, 481 (1970).
 - [10] R. H. Stolen, *Phys. Chem. Glasses* **11**, 83 (1970).
 - [11] E. Whalley, *Trans. Faraday Soc.* **68**, 662 (1972).
 - [12] U. Strom and P. C. Taylor, *Phys. Rev. B* **16**, 5512 (1977).
 - [13] K. K. Mon, Y. C. Chabal, and A. J. Sievers, *Phys. Rev. Lett.* **35**, 1352 (1975).
 - [14] M. A. Bösch, *Phys. Rev. Lett.* **40**, 879 (1978).
 - [15] F. J. Walker and A. C. Anderson, *Phys. Rev. B* **29**, 5881 (1984).
 - [16] S. K. Kazanskii, *JETP Lett.* **41**, 224 (1985).
 - [17] D. G. Cahill and R. O. Pohl, *Phys. Rev. B* **39**, 10477 (1989).
 - [18] S. P. Love, W. P. Ambrose, and A. J. Sievers, *Phys. Rev. B* **39**, 10352 (1989).
 - [19] J. Jäckle, *Z. Phys.* **257**, 212 (1972).
 - [20] See Appendix A in R. W. Alexander, A. E. Hughes, and A. J. Sievers, *Phys. Rev. B* **1**, 1563 (1970).
 - [21] Again, as for the mixed crystals, temperatures above 15 K have not been used because of similar thermally activated relaxation processes at high temperatures.