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Temperature dependence of homogeneous spectral widths of the ^2E-$^4A_2$ transition of Cr^{3+} in silver β-alumina

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Fluorescence line narrowing was used to measure the homogeneous broadening of the ^2E-$^4A_2$ transition of Cr^{3+} ions in Al(1) sites, within the spinel blocks, of crystalline silver β-alumina. The homogeneous linewidth increases as $T^{1.74}$ in the temperature range 7–200 K. This temperature evolution is interpreted as being caused by the interaction between impurity ions and two-level systems, as usually observed in glasses. The glasslike behavior of β-alumina is related to disorder which is present in the conduction planes and which is the origin of the superionic conductivity of this compound.

I. INTRODUCTION

The homogeneous linewidth of optical transitions of impurity ions in crystals is due to processes involving phonons of the host lattice. When the Raman processes are dominant, a T^2 temperature dependence is observed at temperatures $T \geq T_D$, where T_D is the Debye temperature of the crystal. At lower temperatures the T dependence is stronger (a T^7 temperature dependence is expected for T approaching 0 K).[1]

In glasses the mechanisms which give rise to homogeneous broadenings of the emission lines are more complex, and produce much stronger effects than in crystals, leading to an unusual temperature dependence of the linewidths ($\Gamma \approx T^x$, with x ranging typically between 1 and 2).[2] The anomalous behavior of glasses is currently discussed and accounted for by phenomenological models based on two-level systems (TLS's),[3–5] which are typical of amorphous materials. In these systems, the impurity ion, during its relaxation, can exchange energy with the TLS's, as well as with bath phonons. The exponent x depends on several parameters, which usually are difficult to control: they are, for instance, the form of the interaction between the impurity ion and the TLS's, the density of states of the latter, and that of the host matrix.

There is no microscopic model which can describe the TLS's in terms of the defective structure of disordered solids. On the other hand, it would be useful to test the theories for the T dependence of the homogeneous broadening with the help of structurally well-characterized systems. The family of β-aluminas, i.e., the binary compounds of M_2O (M = Na, Ag, K, Rb, Tl, typically) and Al_2O_3, can play an interesting role in this regard: in fact, it provides a set of crystalline compounds (space group $P6_3/mmc$) in which disordered planes (mirror planes) alternate with 11.3-Å-thick ordered crystalline slabs of Al_2O_3 with the spinel structure. The mirror plane is populated by metal cations and oxygen anions, which bridge together two adjacent spinel blocks. The bridging oxygens form a honeycomb network which allows for three unequivalent sets of sites (Beevers-Ross, anti-Beevers-Ross, and mid-oxygen) available to cations.[6] The partial, nonuniform occupation of these sites by cations is the main cause of the disorder present in the conduction planes in β-aluminas. Additional disorder in these planes arises from the lack of stoichiometry in as-grown crystals; the resulting compounds show remarkable bidimensional ionic mobilities, so that these materials constitute a family of very promising solid electrolytes.[7]

Among other isomorphs, sodium β-alumina is the most studied and better characterized one both from the structural and from the dynamical point of view.[8,9] Because of their high mobility, sodium ions can be easily replaced at moderate temperature by other monovalent cations. In general, the derivatives of Na β-alumina show characteristic cation organizations and different degrees of order in the conduction plane, which are temperature dependent. So, for example, at very low temperature silver β-alumina locates the mobile cations preferentially in Beevers-Ross (BR) and in anti-Beevers-Ross (ABR) sites, with few Ag^+ ions in mid-oxygen (MO) sites,[10] showing a considerably different site-occupation degree from that of Na^+ β-alumina.[8] In any case, when the temperature increases the distribution of mobile cations becomes progressively more disordered until it approaches that of a two-dimensional liquid.[11]

Because of their peculiar structure and dynamics, these compounds are the ideal systems for studying the homogeneous linewidth of optical transitions in disordered solids. As a matter of fact, impurity ions can be easily inserted in a β-alumina crystal, either inside the spinel block during the crystal growth, or in the conduction-plane sites, via ionic exchange reactions. Optically active ions can partially replace, within the spinel blocks, Al^{3+} ions, which are both octahedrally and tetrahedrally coordinated to next-neighboring oxygen atoms. So, for example, Cr^{3+} ions enter substitutionally for Al^{3+} ions in octahedral sites, where they show luminescence spectra associated with the ^2E-$^4A_2$ transition with typical shapes and decay times.[12] Moreover, they experience different static and dynamical effects due to the disordered arrangement of mobile cations in the conduction planes.

Cr^{3+} ions in Al(4) sites, at the center of the spinel block and relatively far away from the conduction planes, show emission spectra typical of Cr^{3+} ions in octahedral sites with the ^2E-$^4A_2$ transition split in two lines by the trigonal component of the crystal field. The inhomogeneous broadening of these lines is less than their splitting values, and the spectra are rather insensitive to the mobile cation species of the conduction plane.[13,14]

On the contrary, Cr^{3+} in Al(1) sites, located close to the conduction plane, is more sensitive to the specific disordered arrangement of different cations in β-alumina.[13,14] Therefore, the measurement of the homogeneous linewidth as a function of temperature can give useful information on the dynamical interaction of these impurity centers with the mobile ion sublattice.

Hereafter we shall report on a study of the temperature dependence of the homogeneous broadening of the ^2E-$^4A_2$ transition of Cr^{3+} ions in the Al(1) sites of silver β-alumina. A behavior similar to that observed in glasses is found, thus gaining new, independent evidence which supports the hypothesis[15] of a glasslike structure and dynamics of this crystalline material.

A brief account of part of this work has been recently presented.[16]

II. EXPERIMENT

The crystal of silver β-alumina:Cr^{3+} used for the present measurements is the same that was studied in Ref. 15. It was intentionally doped with chromium (molar fraction Cr_2O_3:$Al_2O_3 \approx 0.1\%$) during the growth. For the present measurements it was mounted into a temperature-controlled optical cryostat, whose temperature could be controlled within ±1 K.

The luminescence spectra were obtained under excitation by the 514.5-nm line of an Ar^+-ion laser. The contribution from centers with different decay lifetimes was selected by mechanically chopping the laser beam and by detecting the spectra in time resolution. For the fluorescence-line-narrowing (FLN) spectra, a pulsed dye laser, with a 0.2-cm^{-1} linewidth, pumped by an excimer laser was used as selective excitation. The fluorescence was analyzed by a double monochromator (resolution limit of 0.15 cm^{-1}) and detected using the photon counting technique. In FLN measurements a time delay of 20 μs and a temporal window of 4 ms (the lifetime at 14 104.5 cm^{-1} was 1.8 ms at 4.2 K) were employed in order to avoid the stray light.

III. RESULTS AND DISCUSSION

In Fig. 1 we report the time-resolved fluorescence spectra obtained at 78 K under excitation by the 514.5-nm line in the $^4A_2$-$^4T_2$ broad band. The spectrum shown in Fig. 1(a) shows the emission associated with the ^2E-$^4A_2$ transition: zero-phonon lines (ZPL's) and relative phonon sidebands are not well resolved. Spectra shown in Figs. 1(b) and 1(c), obtained under pulsed excitation, show the presence of centers with short ($\tau \approx 1.7$ ms at 78 K) and long ($\tau \approx 47$ ms at 78 K) decay times.

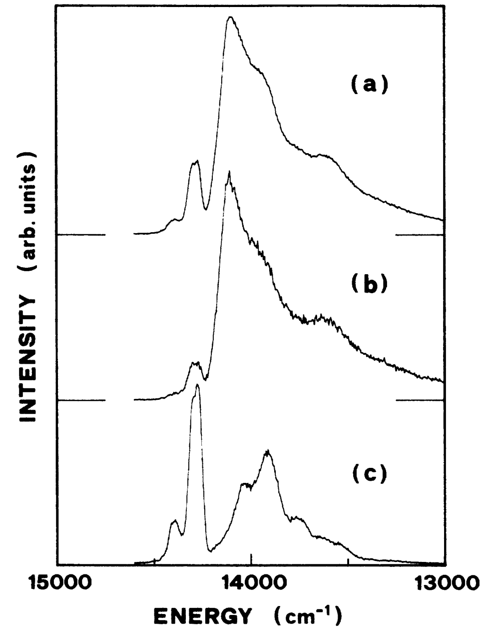

FIG. 1. Luminescence spectra of silver β-alumina:Cr^{3+} crystal at 78 K, obtained under excitation by 514.5-nm laser line: (a) continuous excitation; (b) pulse width $w = 1$ ms and simultaneous detection; (c) $w = 42$ ms and detection from 22 to 50 ms after laser switch-off.

The long-lived luminescence spectrum [Fig. 1(c)], originating from Cr^{3+}-ion emission in the Al(4) site,[12,13] consists of two ZPL's, hereafter referred to as $R1$ and $R2$ in order of increasing energy, and of a well-defined low-energy phonon sideband. The $R1$ and $R2$ ZPL's originate from the splitting of the ^2E state in the low-symmetry crystal field. The very long lifetime is typical of a center with inversion symmetry, for which the optical transition is electric-dipole forbidden.

The short-time spectrum [Fig. 1(b)] consists of a broad band whose linewidth is greater than 100 cm^{-1}. It originates from the ^2E-$^4A_2$ transition of Cr^{3+} ions in Al(1) sites, and its relatively short decay time ($\tau \approx 1.8$ ms at 4.2 K) reflects the absence of inversion symmetry of the occupied site. In this case both the splitting of the ^2E level and the sideband are not resolved because of the large inhomogeneous broadening. As previously reported,[13,14] the spectrum of type 1(c) is not very sensitive either to the nature of or to the temperature-dependent arrangements of mobile cations in the conduction planes. These factors strongly affect the fluorescence from Cr^{3+} ions in the Al(1) sites, and produce quite a broad distribution of the ^2E-$^4A_2$ transition energies.[13,14] However, it is possible to overcome the inhomogeneous broadening and to observe the splitting of both the $^4A_2$ and ^2E states in the low-temperature FLN spectra, by selectively exciting a narrow set of centers inside the broad profile. Typical

FLN spectra, carried out at various experimental resolutions and extending over different energy ranges, are shown in Figs. 2, 3, and 4: these were obtained by excitation at 14 104.5 cm^{-1}, i.e., at the maximum of the inhomogeneous luminescence line.

Figure 2 reports the low-resolution ($\delta\bar{\nu}_{\mathrm{instr}} \approx 3$ cm^{-1}) FLN spectrum, which shows the unresolved resonant ZPL together with its sideband, which is spread over about 900 cm^{-1}. This part of the spectrum contains features which are also observed in the vibrational spectra of the crystal.[17] A direct comparison with the Raman or infrared spectra is not possible, since in these experiments, only the scattering from phonons with nearly zero wave vector is observed, while in our case phonons from the whole Brillouin zone should be coupled with the ${}^2E$-${}^4A_2$ transition. However, the relatively more intense band centered at ≈ 20 cm^{-1} from the resonant ZPL, with a shoulder at ≈ 50 cm^{-1} (see Fig. 3), reflects the splitting of the ${}^2E$ level. In fact, when we excite the system at a given energy within the inhomogeneous profile, two sets of centers will be selected, whose $R1$ or $R2$ lines are resonant with the exciting energy. At very low temperature, this last set of centers quickly relaxes to the lower excited level, from which the $R1$ line originates, and subsequently it emits at a different energy. The large width of the peak shows that the energy spreading of the ${}^2E$ splitting is comparable with the splitting itself. On the other hand, it should be noted that optical phonons in the energy range of 20 cm^{-1} have been observed in silver β-alumina.[17,18]

In order to discriminate between electronic and vibrational contributions, one usually compares FLN spectra recorded after excitation in different parts of the homogeneous profile. In particular, by excitation in the low-energy edge of the band, only $R1$ absorption should occur. This method does not work very well in our case because the electronic splitting (about 20 cm^{-1}) is too small with respect to the inhomogeneous linewidth of the band ($\Gamma_{\mathrm{inho}} > 100$ cm^{-1}), which, furthermore, has a long tail toward low energy. However, on the basis of the present data we are not able to isolate the electronic contribution from that of the vibrational sideband, and therefore we cannot derive the effective density of states of the host crystal which interacts with our impurity centers.

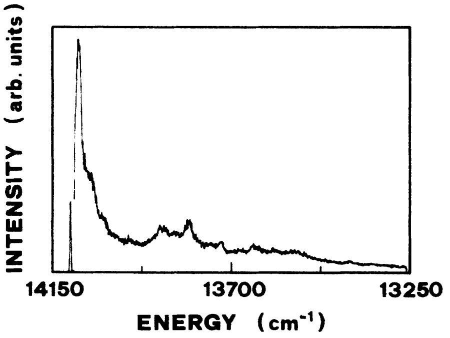

FIG. 2. FLN spectrum obtained at 4.2 K by exciting at 14 104.5 cm^{-1}. The resonant line is reduced by a factor 100. Instrumental resolution (laser-plus-spectrometer linewidth) is about 3 cm^{-1}.

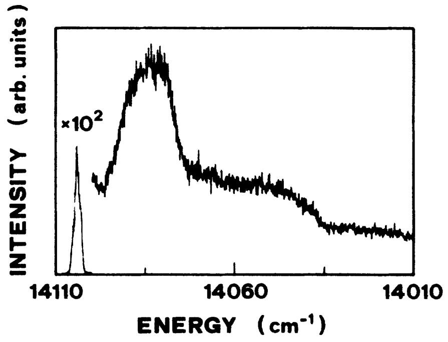

FIG. 3. As in Fig. 2, but with improved resolution (≈ 1 cm^{-1}), and limited to the first 100 cm^{-1} from the resonant line, showing the energy distribution of the ${}^2E$ splitting.

The splitting of the ${}^4A_2$ ground state is well resolved in the spectrum shown in Fig. 4(a), where two satellite lines are coupled with the resonant line, with an energy shift of about 1 cm^{-1}. The width of the central component is the convolution of the instrumental resolution with the homogeneous linewidth. At 4.2 K, however, the homogeneous linewidth is negligible. The two satellite lines appear to be broader than the central line, reflecting an energy spread in the ground-state splitting. By increasing the temperature, the linewidths become larger and larger until the central line masks the two satellites [see Figs. 4(b) and 5]. At higher temperature, moreover, the band at 20 cm^{-1} also contributes to the spectrum: its contribu-

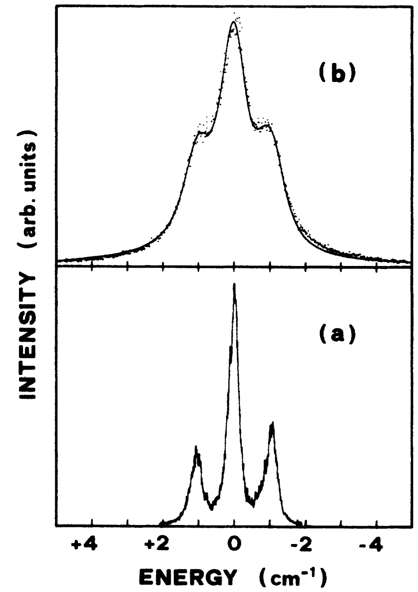

FIG. 4. FLN spectra of the ${}^2E$-${}^4A_2$ transition on Cr^{3+} ions in Al(1) sites of a Ag β-alumina crystal at (a) 4.2 K and (b) 13.2 K, respectively. The laser excitation energy is 14 104.5 cm^{-1} for both spectra. The smooth curve on spectrum (b) is obtained by convolution of a Lorentzian shape with the three-peaked spectrum of Fig. 4(a), corrected for the temperature-dependent populations of the two ground-state sublevels. The instrumental resolution is 0.3 cm^{-1}.

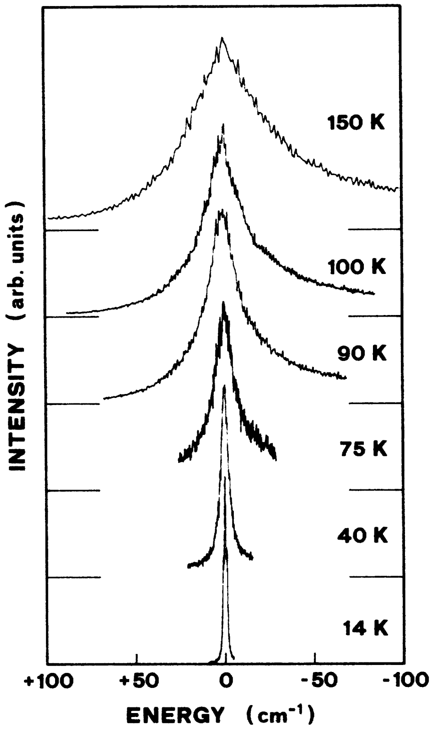

FIG. 5. FLN spectra at different temperatures, obtained by exciting at 14 104.5 cm^{-1}.

tion appears as a shoulder which is more intense on the side of lower energy, and produces an asymmetrical line shape. This fact, however, does not prevent measurement of the homogeneous linewidth with good accuracy. The fitting procedure of the experimental data is based on the convolution of a Lorentzian shape with the three-peaked spectrum of Fig. 4(a). However, the relative populations at the two ground-state sublevels are temperature dependent: in the low-temperature spectra the Stokes-shifted line appears to be more intense than the anti-Stokes one. The T dependence of the relative intensities of the three lines has been studied between 1.5 and 10 K. The three-peaked spectrum used in the convolution procedure has been therefore corrected for its temperature dependence. In Fig. 4(b) we show the results of such a procedure (continuous curve) applied to the FLN spectrum carried out at 13.2 K (dotted curve).

The homogeneous linewidth, which is half the Lorentzian linewidth which provides the best fit, is plotted versus T in a log-log scale in Fig. 6: the behavior over the whole T range is least-squares fitted in terms of a power law, $\Gamma \propto T^x$, with $x = 1.74 \pm 0.07$.

Let us now discuss our results in terms of the current models for the homogeneous line broadening in disordered systems. In a crystalline material the dominant contribution to homogeneous broadening comes from Raman scattering processes by phonons at the impurity center. Its T dependence is very strong ($\Gamma_R \propto T^7$) for $T \ll T_D$, where T_D indicates the Debye temperature of the compound, and approaches to a T^2 law for $T \gg T_D$. One-phonon processes are also important in the low-temperature regime, when ground or excited electronic states are split (in our case they are both split). However, their contribution should be comparable to that observed in ruby,[1,19] and indeed completely negligible.

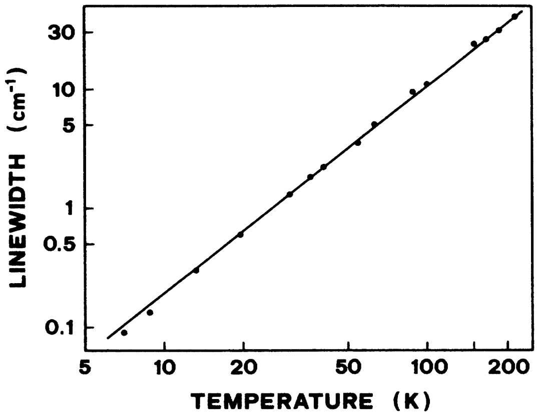

FIG. 6. Homogeneous linewidths vs temperature for the ^2E-$^4A_2$ transition of Cr^{3+} ions in Al(1) sites in a Ag β-alumina crystal, excited at 14 104.5 cm^{-1}. The data are fitted by a straight line with slope 1.74±0.07.

The linewidth of Cr^{3+} in β-alumina is more than an order of magnitude higher than in ruby,[1,19] in the whole temperature range sampled, and is also higher than in the mullite glass.[20] Moreover, we measure a slope lower than 2, a result which is usually found in glasses. These considerations suggest that the dominant mechanism responsible for the broadening is the same as in the "true" glasses, where the elementary excitations connected with the structural disorder (TLS's) strongly couple to optical impurities. Low-energy excitation modes, other than phonons, have been found in β-alumina crystals in low-temperature thermal measurements,[21-23] which exhibit the same anomalies as those observed in glasses and in polymers.[24,25] A nearly energy-independent density of TLS's has been postulated to occur in β-alumina, due to the glasslike structure of its conduction plane. Therefore, although it is a crystalline compound, we can try to use the same models developed for glasses in order to account for the measured T dependence of the homogeneous broadening. According to these models, the resulting linewidth is the sum of the individual widths due to interactions of optical centers with each TLS. An average is carried out over the TLS's parameters, such as the asymmetry of the double-well potential, the tunneling matrix element, and the strength of the interaction V which is assumed to have a multipolar character ($V \approx r^{-s}$, with $s=3$ for dipole-dipole and $s=4$ for dipole-quadrupole interactions, respectively).[5] In a homogeneous glass a uniform distribution of TLS states is assumed: in our system the defect structure is confined in planar regions 11.3 Å apart from each other.[6,10] However, for dipole-dipole and for dipole-quadrupole interactions, it has been found that a large number of TLS's are active. Because of the long-range nature of such an interaction, the assumption of a homogeneous spatial distribution of TLS states in β-alumina should not be too bad an approximation. The expected slope in the ($\log\Gamma$)-($\log T$) plot is $x = 1 + \mu + \tilde{d}(1-3/s)$, where μ gives the density of states of TLS's $\rho(E) = E^{\mu}$, s measures the strength of the TLS–impurity-centers interaction $V(r)=r^{-s}$, and $\tilde{d}$ gives the spectral dimension of the coupling vibrations.[4] As for the nature of the interaction, it is reasonable to assume the TLS's behave as dipoles, if they are related to the motion of Ag^+ ions among inequivalent sites of the conduction plane, while the ^2E-$^4A_2$ transition of the Cr^{3+} ion should have comparable dipole and quadrupole characters. The measured slope for the temperature dependence of the linewidth is well reproduced assuming a dipole-quadrupole interaction with a flat density of TLS's ($\mu=0$), and mediated by phonons ($\tilde{d}=3$); this results in $x=1.75$, which is quite close to the measured value. However, we want to point out that $\tilde{d}$ values different from 3 should not be rejected *a priori*, due to the possible localization of the vibrations in the disordered region of the conduction plane.

IV. CONCLUSIONS

Our FLN measurements show that the homogeneous broadening of the emission lines of Cr^{3+} ions in spinel-block Al(1) sites in silver β-alumina shows a behavior which is similar to that observed in glasses. This result is both interesting and intriguing at the same time. In fact, the system shows a crystal structure, made up by ordered spinel blocks;[6] such a crystal structure is reflected by the Raman spectrum,[18] whose high-frequency features are characteristic of a typical phonon spectrum with sharp and well-shaped peaks. Nevertheless, the interaction between optical impurities and the dynamics of the defective structure of the conduction planes turns out to be the dominant mechanism responsible for the homogeneous broadening of the emission lines. The system looks very promising in view of further optical spectroscopy measurements in disordered media. In fact, it is possible to change some parameters such as the content of mobile cations in the conduction planes, either by partial or by total ion replacement. Moreover, the impurity ions (transition-metal or rare-earth elements) can be introduced either in spinel-block sites [Al(4) and Al(1) sites, as in our crystal], or in the conduction-plane sites (BR, ABR and MO sites, as was done in sodium β''-alumina crystals[26,27]), with different degrees of coupling with the mobile-cation sublattice.

In this respect, β-aluminas are much more interesting than glasses, where there are only minor possibilities of controlling the parameters which affect the interaction between optical centers and TLS states. Finally, in the case of β-aluminas, it should be very interesting to correlate the microscopic nature of TLS's with the diffusional dynamics of the mobile cations among the nearly equivalent sites of the conduction plane, and, therefore, to try to connect the observed homogeneous broadenings to ionic conductivity data.

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