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Electron spin resonance spectra of Gd^{3+} ions in K_2SO_4–$ZnSO_4$ glasses

B. SREEDHAR, J. LAKSHMANA RAO, S. V. J. LAKSHMAN
Department of Physics, Sri Venkateswara University, Tirupati 517502, India

Electron spin resonance (ESR) spectra of Gd^{3+} ions doped in K_2SO_4–$ZnSO_4$ glasses have been studied on an X-band ESR spectrometer at different temperatures (−120 to 150° C). The ESR spectrum at room temperature exhibits three prominent features with effective **g**-values of ~ 5.6, 2.83 and 2.02. The spectra are similar to the "U" spectra familiar in many oxide and fluoride glasses, indicating very low and disordered site symmetries with a broad distribution of crystal fields. Remarkable changes have been observed in the spectrum with changes in the temperature, concentration and glass composition. The broadening of the $g \sim 2.02$ line with increasing Gd^{3+} ion content indicates that the dipole–dipole interaction between the resonant centres increases with increase in Gd^{3+} ion content. A weak band at 36 350 cm^{-1} is observed in the optical absorption spectrum of 0.5 mol % Gd^{3+} in K_2SO_4–$ZnSO_4$ glass which has been assigned to the transition $^8S_{7/2} \rightarrow {}^6P_{7/2}$.

1. Introduction

In recent years there has been considerable activity in the research on common glasses and other less-common non-crystalline solids containing rare-earth ions, because the rates at which, and the mechanism by which, excited states of rare-earth ions form and decay are of great importance in the application of these ions in phosphor, laser and other currently developed electronic devices. Compared with transition metal ions, the electron spin resonance (ESR) of rare-earth ions (Gd^{3+} and Eu^{2+}) in glassy solids has been far less extensively studied, although there has been a considerable number of investigations in the ultraviolet-visible region aimed at evaluating parameters associated with the lasing action of these ions in glassy solids [1].

Investigations on the phase diagram studies [2] of K_2SO_4–$ZnSO_4$ glasses reveal that these glasses can be obtained over a wide range of binary compositions. ESR spectra of transition metal ions [3–6] in K_2SO_4–$ZnSO_4$ system of glasses were studied by various authors and they concluded that the transition metal ions go substitutionally to zinc ion sites which are octahedrally coordinated with sulphate ions. In the present work, we describe the ESR results obtained for K_2SO_4–$ZnSO_4$ glasses doped with trivalent gadolinium ions.

2. Experimental procedure

The starting materials of this study were analar grade K_2SO_4, $ZnSO_4$ and $GdNO_3$. After weighing in a micro-analytical balance, the materials in the following proportions were prepared:

(i) $xK_2SO_4 \cdot (1 - x - y)\ ZnSO_4 \cdot yGd_2O_3$; $0.0025 < y < 0.02$ in steps of 0.0025 and $x = 0.7$.

(ii) $xK_2SO_4 \cdot (1 - x - y)\ ZnSO_4 \cdot yGd_2O_3$; $y = 0.006$ and $x = 0.4$, 0.5 and 0.6.

The materials were mixed thoroughly and kept in a muffle furnace at about 350° C for nearly 3 h to convert $GdNO_3$ to Gd_2O_3; the temperature of the furnace was then raised to 750° C; the melt was kept in the furnace for about 4 h and was then quickly poured and quenched on a plane surface.

ESR spectra were recorded on a Jeol-FE1X ESR spectrometer operating in the X-band frequencies with field modulations of 100 kHz. The microwave frequency was set at 9.205 GHz and the magentic field was scanned between 0 and 5000 G. The ESR spectra were also recorded in the temperature range −120 to 150° C, to study the temperature dependence of the intensities of the resonance lines.

Optical absorption spectrum was recorded at room temperature on a Perkin-Elmer 551 spectrometer in the wavelength region 250 to 400 nm.

3. Results and analysis

In undoped samples no ESR signal is detected. When Gd^{3+} ion is introduced into the K_2SO_4–$ZnSO_4$ glasses, all samples exhibit absorption lines. Fig. 1 shows the ESR spectrum of Gd^{3+} ion in K_2SO_4–$ZnSO_4$ glass at room temperature obtained for 0.5 mol % Gd_2O_3. The ESR spectrum shows three prominent features with effective g values of ~ 5.6, 2.83 and 2.02. The spectrum is similar to that observed by earlier workers in a variety of glasses doped with Gd^{3+} ion, e.g. methanol glass [7], borate glasses [7–9], phosphate glasses ($ZnO.P_2O_5$) [8, 10], chalcogenide ($Tl_2SeAs_2Se_3$) glass [10], silicate glasses [11–13], fluoride glass [14] and fluorozirconate glass [15].

ESR signals in glasses show a reasonable concentration dependence. As the Gd^{3+} ion content is increased, the intensities as well as the linewidth of the resonance peaks are increased. The ESR signal at **g** $= 2.02$ is broadened very much and this shows that

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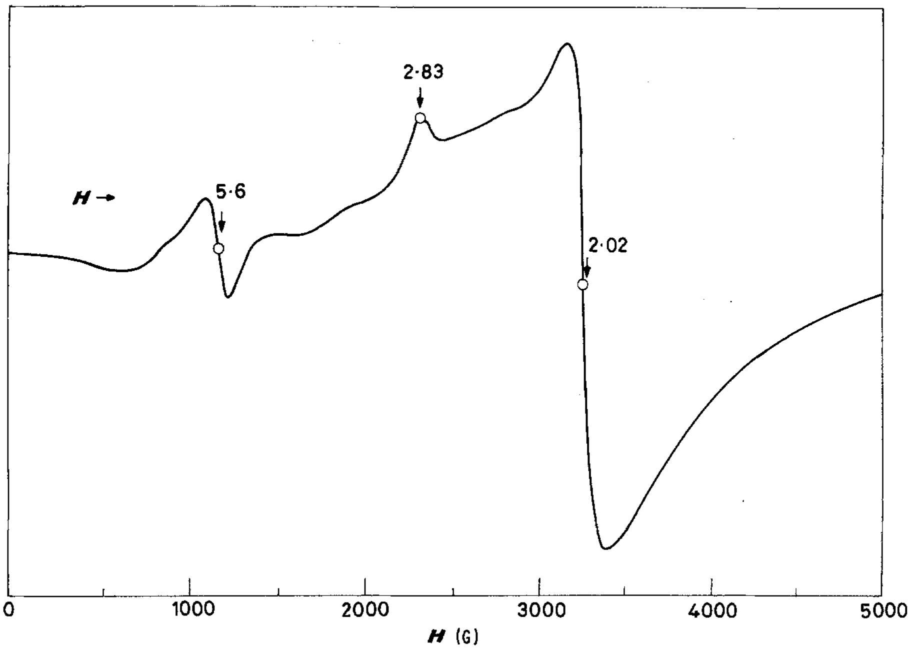

Figure 1 ESR spectrum of 0.5 mol % Gd^{3+} ions in K_2SO_4–$ZnSO_4$ glass at room temperature.

the dipole–dipole interaction between the resonant centres increases as the Gd^{3+} ion content is increased [16].

From the first derivative resonance curve, the relative intensity (I) and the peak-to-peak width (ΔH_{pp}) are estimated. The number of spins (N) participating in the resonance are roughly estimated by the equation [17]

$$N = I(\Delta H_{pp})^2$$

under the assumption that the intensities of the resonance per unit number of Gd^{3+} ions equal each other.

Fig. 2 shows the increase in the peak-to-peak height (I) at the two resonances (i.e. $g = 5.6$ and 2.02) as a function of Gd^{3+} ion content. The dependence of relative intensities upon the Gd^{3+} ion content for $I_{g=5.6}$ and $I_{g=2.02}$ resonance lines are shown in Fig. 3. The variation of the peak-to-peak width (ΔH_{pp}) and the Gd^{3+} ion content are plotted in Fig. 4. This variation in the peak-to-peak width (ΔH_{pp}) with increase in Gd^{3+} ion content in the host glass is due to the increase in the dipole–dipole interaction between the resonant centres [16].

Remarkable changes have been observed in the spectrum when the composition of the K_2SO_4–$ZnSO_4$ glass is changed. As the $ZnSO_4$ content is increased, the intensities of both the resonance signals at $g = 5.6$ and 2.02 are decreased. Fig. 5 shows the variation of peak-to-peak height (I) at the two resonances ($g = 5.6$ and 2.02) as a function of $ZnSO_4$ content. The decrease in the intensities of the resonance lines at $g = 5.6$ and 2.02, as the $ZnSO_4$ content in K_2SO_4–$ZnSO_4$ glasses is increased, may be due to a decrease in the randomness of Gd^{3+} ions in the host glass.

ESR spectra were recorded in the temperature range −120 to 150° C, to study the temperature dependence of the intensities of the resonance lines. With increasing the temperature from −120° C the intensities of the resonance lines decreased gradually in proportion to the Boltzman factor. This fall in intensity, with increase in temperature can be attributed to relaxation broadening. ESR spectra at different temperatures are shown in Fig. 6. From the figure, it is clear that the intensities of the resonance lines at $g = 5.6$ and 2.02 are decreased with increase in temperature. The temperature dependence of the peak-to-peak height ($I_{g=5.6}$ and $I_{g=2.02}$) for 0.5 mol % Gd^{3+} ions is plotted in Fig. 7.

In Fig. 8, the number of Gd^{3+} ions participating at

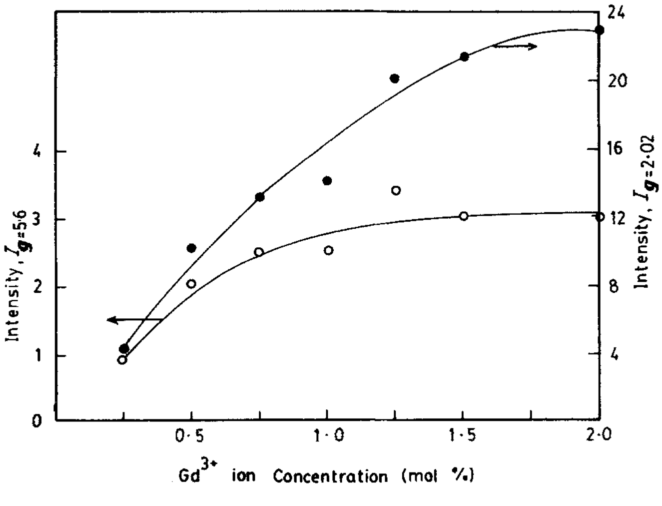

Figure 2 Dependence of the peak-to-peak height (I) at the two resonances, i.e. $g = 5.6$ and 2.02, as a function of Gd^{3+} ion content.

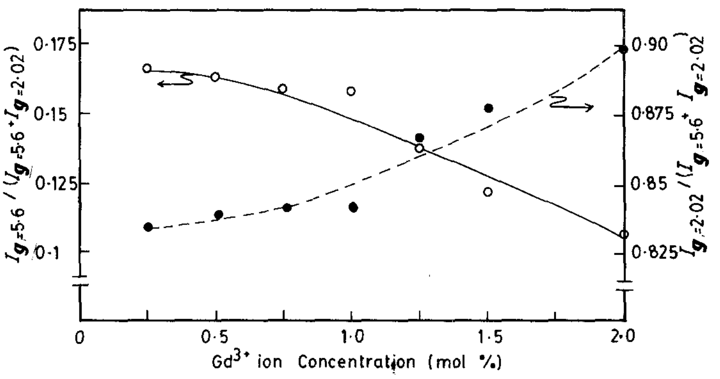

Figure 3 Dependence of the relative intensity (i.e. $[I_{g=5.6}/(I_{g=5.6}+I_{g=2.02})]$ and $[I_{g=2.02}/(I_{g=5.6}+I_{g=2.02})]$ upon the Gd^{3+} ion content.

the two resonances ($N_{g=5.6}$ and $N_{g=2.02}$) are given as a function of temperature. In both cases, the number of Gd^{3+} ions participating in the resonance decreases monotonically when the temperature is increased from -120 to 150° C. Fig. 9 shows the temperature dependence of relative quantities $r_{g=5.6} = [=N_{g=5.6}/(N_{g=5.6}+N_{g=2.02})]$ and $r_{g=2.02} = [=N_{g=2.02}/(N_{g=5.6}+N_{g=2.02})]$ for Gd^{3+} ions in K_2SO_4-$ZnSO_4$ glass at different temperatures.

The optical absorption spectrum recorded at room temperature exhibits a weak band at $36\,350\,cm^{-1}$ (275 nm). This band has been attributed to the transition $^8S_{7/2} \rightarrow {}^6P_{7/2}$.

4. Discussion

ESR spectra of rare-earth ions in glassy solids are generally very anisotropic and sensitive to variations in ligand field from site to site. Owing to this, the ESR spectra of Gd^{3+} ions in glassy solids are far less extensively studied. ESR spectrum of Gd^{3+} ions in glasses is characterized by three prominent features with effective g-values of ~ 6.0, 2.8 and 2.0 with weaker features at $g = 3.4$ and 4.7. This type of spectrum has been aptly labelled the U-spectrum [18] in view of its omnipresence in vitreous materials [19–22] as well as in disordered polycrystalline materials [18, 23, 24]. To date, the correct interpretation of the U-spectrum has been the subject of considerable controversy.

Chepeleva and Lazukin [25] were the first to interpret the U-spectrum. The $g \sim 6.0$ feature of the U-spectrum was attributed to a strong cubic field on the basis of the solutions obtained for a "cubic" Hamiltonian in the strong crystal field limit where the Zeeman interaction may be treated as a perturbation.

Later, Nicklin *et al.* [19] searched extensively for a single set of "rhombic" crystal field parameters that could simultaneously account for all the principal features of the U-spectrum, but they attributed the three prominent features to a distinct type of crystal field. The $g \sim 6.0$ feature was attributed to a strong cubic crystal field, as in the Chepeleva and Lazukin [25] interpretation.

Both Cugunov and Kliava [22] and Koopmans *et al.* [26] employed computer simulation techniques in their analysis, but their final interpretations are distinctly different. Cugunov and Kliava [22] have attributed the $g \sim 6.0$ feature to a strong and well-defined rhombic crystal field and the broad resonance encompassing $g \sim 2.0$ arising from clusters of Gd^{3+} ions, whereas Koopmans *et al.* [26] have assigned the $g \sim 6.0$ feature to intermediate crystal field strength site of axial symmetry, and have attributed the broadened general appearance of the U-spectrum to isolated rare-earth ions at a wide variety of sites.

Recently, Broadbeck and Iton [27] have systematically analysed the previous interpretations of the U-spectrum on the basis of a set of criteria and found all the four previous interpretations of the ESR spectra to be unsatisfactory. By taking into consideration a wide range of ESR and optical data, and *ab initio* computer simulations of the ESR spectra, they concluded that glassy or disordered host materials impose virtually no specific or narrowly defined site symmetries on the rare-earth ions, with the result that the rare-earth ions can coordinate themselves with a relatively large number of irregular disposed ligands. Also the U-spectrum is expected to prevail only when the coordination number of the rare-earth cations is high, i.e. $\geqslant 6$ within the matrices that are structurally disordered or which allow irregular occupancy of

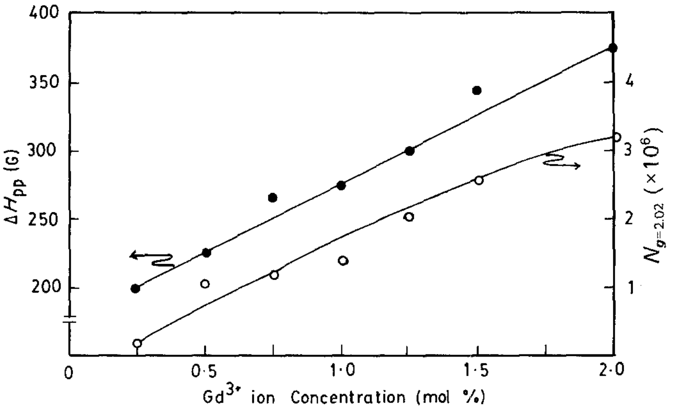

Figure 4 Linewidth of $g = 2.02$ resonance, and the number of Gd^{3+} ions participating at $g = 2.02$, i.e. $N_{g=2.02}$ plotted against Gd^{3+} ion content.

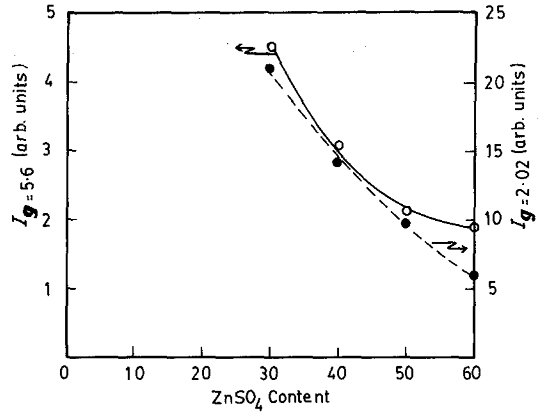

Figure 5 Dependence of the peak-to-peak height (I) at $g = 5.6$ and 2.02 as a function of ZnSO$_4$ content.

nearby sites by chemically inequivalent ions. The site symmetries of the rare-earth ions are essentially low and disordered, and are best characterized by a single low-symmetry glassy site as proposed by Griscom [28].

The interpretation of the U-spectrum which is due to a broad distribution of site symmetries, contrasts markedly with results of iron group ions, in oxide [28], fluoride [29, 30] and sulphate glasses [3–6], where a more precisely defined site symmetry, usually octahedral, is normal. From the ESR spectra of paramagnetic ions in K_2SO_4–$ZnSO_4$ glasses, various authors [3–6] have concluded that the site symmetry around the paramagnetic ion is octahedral and goes substitutionally at zinc ion sites. On the other hand, the glass structure imposes no such simple symmetry on the rare-earth ions with their ionic size. It appears that the Gd^{3+} ion in K_2SO_4–$ZnSO_4$ glass "dictate" their own environments and occupy sites surrounded by polyhedra of more of less irregularly distributed sulphate ligands with a high coordination number $\geqslant 6$.

Theoretically, the admixture of the $^6P_{7/2}$ state to the ground state can be written as $(1 - \alpha^2)^{1/2}\,{}^8S_{7/2} + \alpha^2\,{}^6P_{7/2}$, where α is a measure of the amount of admixture [31]. The g-value of this state is then

$$g = (1 - \alpha^2)g(^8S_{7/2}) + \alpha^2 g\,(^6P_{7/2}) \qquad (1)$$

where $g\,(^8S_{7/2}) = 2.0023$ and $g\,(^6P_{7/2}) = 12/7$. In accordance with Baker and Williams [32] we take

$$\alpha^2 = 14\,\frac{\xi^2}{W_P^2} \simeq 0.2433$$

where ξ is the one electron spin-orbit coupling parameter equal to $1534\,\text{cm}^{-1}$ [33], and W_p is the energy difference between $^8S_{7/2} \rightarrow {}^6P_{7/2}$ ($W_p = 36350\,\text{cm}^{-1}$). Inserting the value of α^2 into Equation 1, we obtain $g = 1.93$ which is close to the value of g within experimental accuracy.

5. Conclusion

The spectra observed in the present work are very similar to the U-spectra reported for Gd^{3+} ions in many oxide and fluoride glasses. From the ESR spectra of Gd^{3+} ions in K_2SO_4–$ZnSO_4$ glasses, the authors conclude that the glass structure imposes no simple symmetry and the Gd^{3+} ions dictate their own environment in glass and occupy sites surrounded by polyhedra of more or less irregularly distributed sulphate ligands with high coordination number $\geqslant 6$.

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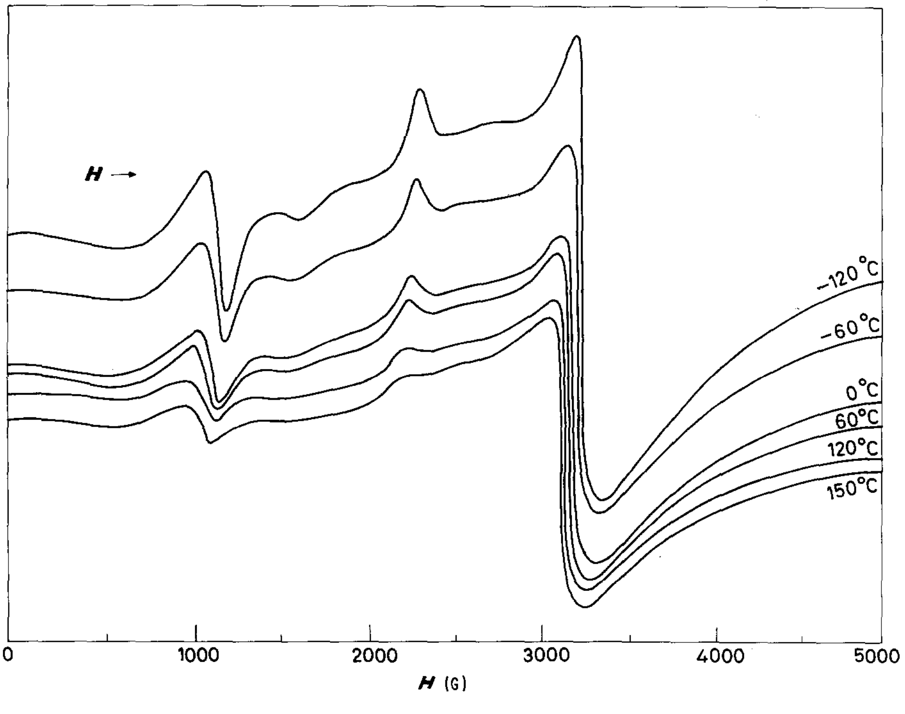

Figure 6 ESR spectra of 0.5 mol % Gd^{3+} ions in K_2SO_4–$ZnSO_4$ glass at different temperatures.

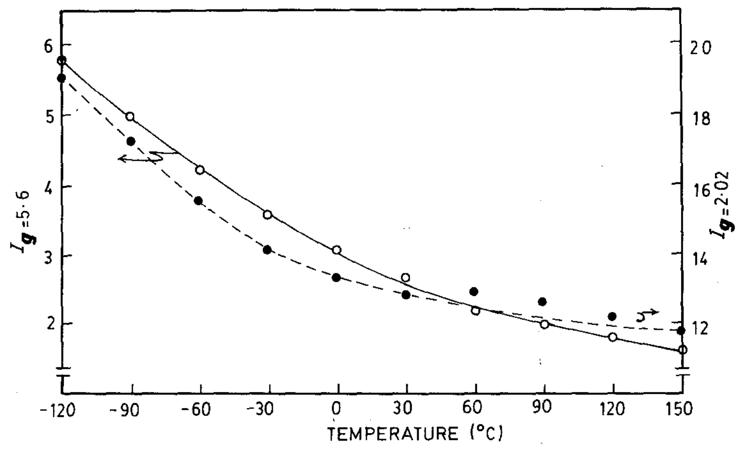

Figure 7 Temperature dependence of the peak-to-peak height (I) (i.e. $I_{g=5.6}$ and $I_{g=2.02}$) for 0.5 mol % Gd^{3+} ions in K_2SO_4-$ZnSO_4$ glass.

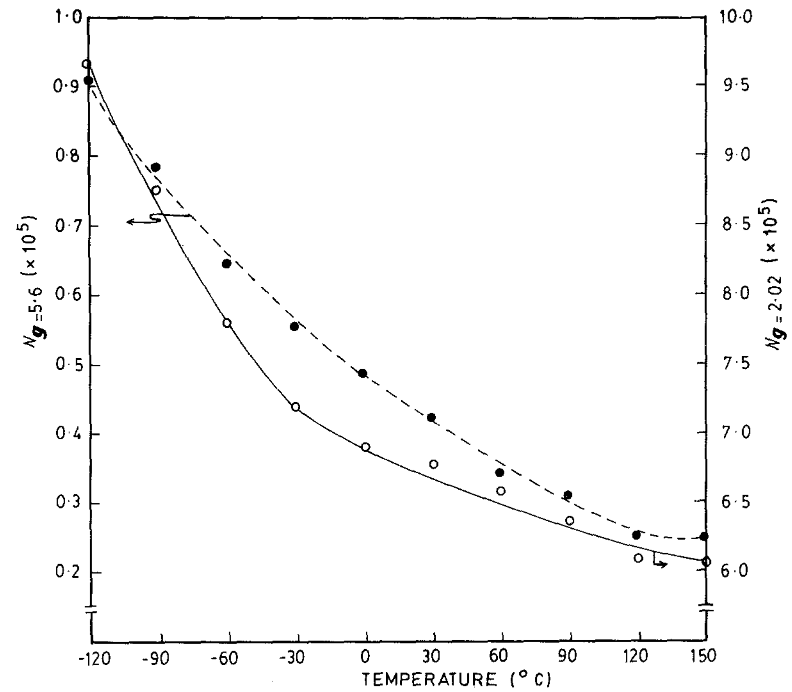

Figure 8 Number of Gd^{3+} ions related to g = 5.6 and g = 2.02 (i.e $N_{g=5.6}$ and $N_{g=2.02}$, respectively) as a function of temperature.

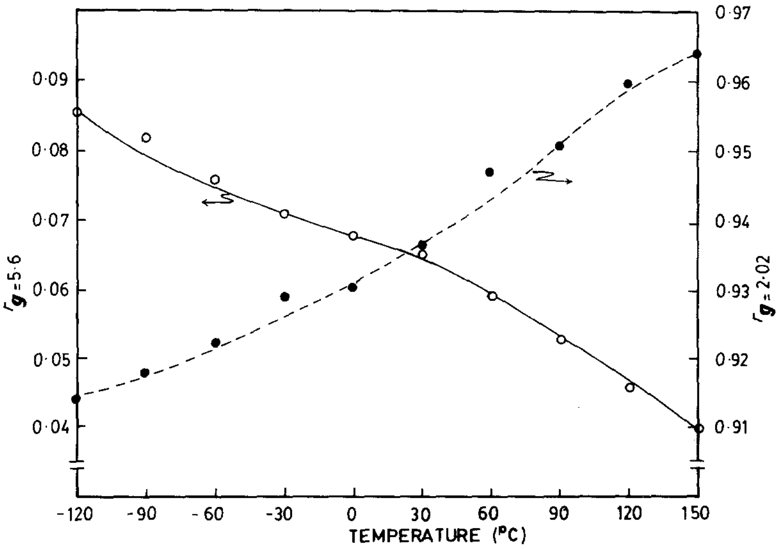

Figure 9 Dependence of relative quantity of Gd^{3+} ions related to g = 5.6 and 2.02 resonances (i.e. $r_{g=5.6}$ and $r_{g=2.02}$, respectively) at different temperatures.

References

1. J. WONG and C. A. ANGELL, "Glass Structure by Spectroscopy" (Marcel Dekker, New York, 1976) p. 149.
2. P. S. L. NARASHIMHAM and K. J. RAO, *J. Non. Crystl. Solids* **27** (1978) 225.
3. H. G. K. SUNDAR and K. J. RAO, *ibid.* **50** (1982) 137.
4. V. P. SETH, V. K. JAIN and R. K. MALHOTRA, *ibid.* **57** (1983) 199.
5. A. YADAV and V. P. SETH, *Phys. Chem. Glasses* **27** (1986) 182.
6. J. LAKSHMANA RAO, B. SREEDHAR and S. V. J. LAKSHMAN, *J. Non-Cryst. Solids* **105** (1988) 95.
7. N. S. GARIF'YANOV, R. KH. TIMEROV and N. F. USACHEVA, *Sov. Phys. Solid State* **4** (1962) 2448.
8. G. G. MSHVELIDZE and KH. I. GAPRIDASHVILI, *ibid.* **13** (1972) 2860.
9. S. SIMON and A. NICUIA, *Phys. Status Solidi A* **81** (1984) K1.
10. G. O. KARAPETYAN, D. M. YUDIN and D. G. GALLIMOV, *Bull. Acad. Sci USSR, Phys. Ser.* **31** (1967) 814.
11. A. NUICUIA and E. TRIF, Proc. Congr. Ampere, 17th, 1973, (1974) p. 543.
12. R. C. NICKLIN, PhD thesis, Iowa State University; published as Technical Report US AEC (1967) IS-T-203.
13. R. P. HUNT and K. N. R. TAYLOR, *J. Mater. Sci.* **8** (1973) 203.
14. Y. YONEDA, H. KAWAZOE, T. KANAZAWA and H. TORATANI, *J. Non-Cryst. Solids* **56** (1983) 33.
15. D. FURNISS, E. A. HARRIS and D. B. HOLLIS, *J. Phys. C* **20** (1987) L147.
16. S. SIMON, A. GIURGIU, T. OETRIGOV and A. NICULA, *Proc. Int. Conf. Magn. Rare-Earth Actinides* **1** (1983) 217.
17. D. M. MOON, J. A. AITKEN, R. M. MAC CRONE and G. S. CIELOSZYK, *Phys. Chem. Glasses* **16** (1975) 91.
18. L. E. ITON and J. TURKEVICH, *J. Phys. Chem.* **81** (1977) 435.
19. R. C. NICKLIN, J. K. JOHNSTONE, R. G. BARNES and D. R. WILDER, *J. Chem. Phys.* **59** (1973) 1652.
20. N. S. GARIYANOV and M. M. ZARIPOV, *Sov. Phys. Solid State* **6** (1964) 1209.
21. I. V. CHEPELEVA, V. N. LAZUKIN and S. A. DEMDOVSKII, *Soviet Phys. Dokl.* **11** (1967) 864.
22. L. CUGUNOV and J. KLIAVA, *J. Phys. C* **15** (1982) L933.
23. L. E. ITON, S. L. SUIB and G. D. STUCKY, *Bull. Magn. Reson.* **2** (1981) 174.
24. L. E. ITON, C. M. BRODBECK, S. L. SUIB and G. D. STUCKY, *J. Chem. Phys.* **79** (1983) 1185.
25. I. V. CHEPELEVA and V. N. LAZUKIN, *Dokl. Akad. Nauk. SSR* **226** (1976) 311.
26. H. J. A. KOOPMANS, M. M. PERIK, B. NIEWEUTHUIJSE and P. J. GELLINGS, *Phys. Status Solidi (b)* **120** (1983) 745.
27. C. M. BRODBECK and L. E. ITON, *J. Chem. Phys.* **83** (1985) 4285.
28. D. L. GRISCOM, *J. Non-Cryst. Solids* **40** (1980) 211.
29. P. W. FRANCE, S. F. CARTER and J. M. PARKER, *Phys. Chem. Glasses* **27** (1986) 32.
30. E. A. HARRIS, *ibid.* **28** (1987) 196.
31. T. OOSTERHOFF and H. W. DEN HARTOG, *Phys. Status Solidi (b)* **62** (1974) 469.
32. J. M. BAKER and F. I. B. WILLIAMS, *Proc. Roy. Soc. A* **267** (1962) 283.
33. B. R. JUDD and I. LINDGREN, *Phys. Rev.* **122** (1961) 1802.

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