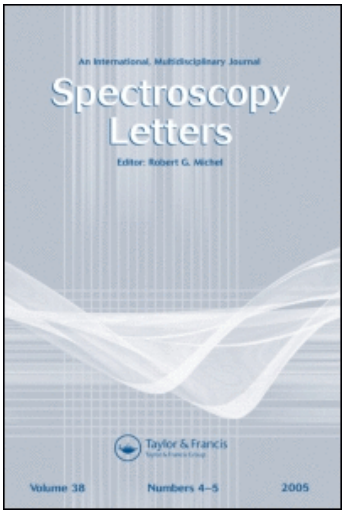

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Stump, Nathan A. , Burns, Jerry B. , Dai, Sheng , Mamantov, Gleb , Young, Jack P. and Peterson, Joseph R.(1993) 'Europium Oxychloride Absorption Spectroscopy as an Optical Probe of Temperature', Spectroscopy Letters, 26: 6, 1073 — 1083
To link to this Article: DOI: 10.1080/00387019308011595
URL: http://dx.doi.org/10.1080/00387019308011595

SPECTROSCOPY LETTERS, 26(6), 1073-1083 (1993)

EUROPIUM OXYCHLORIDE ABSORPTION SPECTROSCOPY AS AN OPTICAL PROBE OF TEMPERATURE*

Key Words: EuOCl, temperature probe, absorption spectroscopy

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ABSTRACT

The temperature dependence of the features which arise from the $^7F_{0,1} \rightarrow {}^5D_3$ absorption transitions in EuOCl as seen by diffuse-reflectance spectroscopy has been investigated. The transitions shift linearly to higher energy with increasing temperature. The ratio of the intensities of the transitions arising from the $^7F_0$ state to those arising from the $^7F_1$ state also appears to be a linear function of temperature.

* Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under grant DE-FG05-88ER13865 to the University of Tennessee, Knoxville and contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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INTRODUCTION

High temperature and extremely low temperature determinations of absorption maxima have proven difficult, inconvenient, or impossible in many cases. However, as discussed in a recent study of the diffuse reflectance spectrum from EuOCl at 77 K,[1] many of the difficulties may be overcome through the use of an all-quartz fiberoptic probe placed in direct contact with the sample. In this previous work, it was suggested that the temperature dependence of the spectroscopic features might be of use as an optical probe of temperature. Spectroscopic methods using diamond,[2] ruby,[3] or a lanthanide compound[4] have been employed in our laboratory for the determination of temperature and/or pressure. In such cases, changes in the positions or intensities of Raman features or in the positions, intensities, or luminescent lifetimes of emission features have been used as indicators of change in the environment (temperature/pressure) in which the compound is placed.

EuOCl is an ideal candidate for use as an environmentally sensitive compound. The compound is structurally and chemically stable in air from liquid helium temperature up to over 1000 K. The invariability of its structure and chemical composition over a wide range of temperature removes the two major contributions which have the greatest effect on the electronic spectrum of a lanthanide material; thus the smaller shifts induced by changes in temperature and/or pressure may be studied and exploited. The electronic spectrum of EuOCl is very well known and is made up of narrow features which can be studied by either absorbance/reflectance or emission spectroscopy. Synthetic procedures to obtain a powdered sample of EuOCl are moderately straightforward. In combination with a remote all-quartz fiberoptic probe, as in this case, the EuOCl temperature probe may be placed in various caustic or inconvenient environments and still facilitate reflectance, Raman, or luminescence spectroscopic determination of temperature.

EXPERIMENTAL DETAILS

A powdered sample of EuOCl was prepared by heating $EuCl_3 \cdot 6H_2O$ in air at 400-450 °C.[5] The crystal structure of the EuOCl sample was confirmed by phonon Raman[6] and Eu^{3+} ion emission patterns.[7] The EuOCl sample was loaded into a quartz tube with an inside diameter of ~4 mm, slightly larger than that of an all-quartz fiberoptic probe which has been described previously.[8,9] Briefly, the construction of the probe entailed the fusion under vacuum of four, 600 μm diameter quartz fibers within a heavy-walled quartz tube (the vacuum prevents the formation of air pockets during the fusion step). Once cooled, the tip of the probe was cut perpendicular to the length of the tube, then polished to a smooth finish with successively finer grades of emery paper. The fiber optic probe was then inserted into the quartz tube in direct contact with the EuOCl sample. The combined apparatus along with a Pt-Pt/10% Rh thermocouple for temperature calibration was then inserted into either an adjustable furnace or a liquid nitrogen cooled air stream. The light from a tungsten lamp (ORIEL, model 66181) was focused through a microscope objective into the end of the single illumination fiber of the probe. The diffuse reflectance was collected by the three remaining fibers and focused upon the entrance slit of a 1-meter double monochromator (Jobin Yvon-Instruments SA, model HG.2S), which has a resolution of 0.5 cm^{-1} at 514.5 nm. The light exiting the monochromator was focused onto a cooled photomultiplier tube (Hamamatsu, model R636). The output of the photomultiplier tube was amplified and processed with standard pulse counting electronics. Data were stored using a multichannel analysis system (Nicolet, model 1170) and processed by means of an AT personal computer using "Spectra Calc" software (Galactic Industries Corp.).

RESULTS AND DISCUSSION

The diffuse reflectance spectra exhibited by the Eu^{3+} ion's $^7F_{0,1} \rightarrow {}^5D_3$ absorption transitions at various temperatures from 77 to 1088 K are shown in Figure 1.

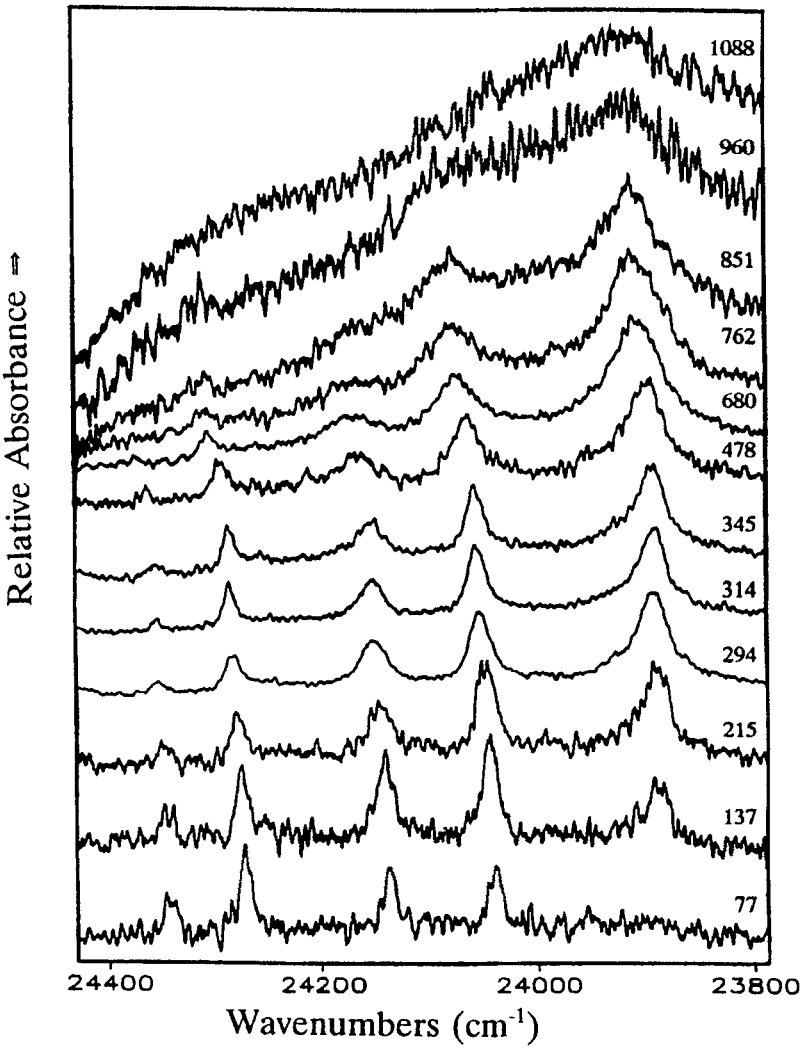

FIG 1. Partial Diffuse Reflectance Spectrum of EuOCl at Various Temperatures (K).

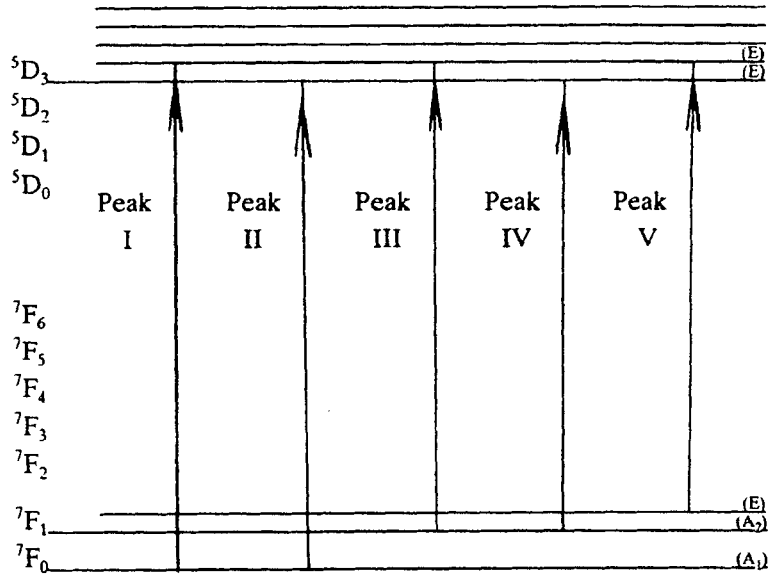

FIG 2. Schematic Diagram of the Eu^{3+} Ion Energy Levels of Interest. (Irreducible Representations are Given in Parentheses)

These transitions are shown schematically in Figure 2 and described in detail in Reference 1. At low temperatures the lowest energy transition disappears due to the lowering of the population of the excited state from which it arises. At high temperatures the thermal noise from the furnace overwhelms the reflectance of the sample. Modulation of the source and lock-in amplification of the sample's reflectance over the constant noise from the furnace might allow for useful measurements at still higher temperatures.

Transition Energy vs. Temperature

The transition energies all shift toward higher energy with increasing temperature (see Fig. 1). It has been suggested by Dieke[10] that shifts in transition energy (peak position) are due to a lessening of the effect of the crystal field, which results from the thermal expansion of the crystal. Thus, as temperature is

increased, the crystal expands, the crystal field at the Eu^{3+} ion site is lessened, and the spectrum approaches that expected for a "free" Eu^{3+} ion.

It was also suggested by Dieke[10] that the shift toward the free ion spectral peak position should exhibit exponential characteristics. This was not observed in the present study. Plots of observed peak position versus temperature for each of the five studied transitions are given in Figure 3. With the exception of the lowest energy transition, a plot of peak position versus temperature is linear. This result may be due to collecting the data over the nearly linear, asymptotic portion of an exponential curve. However, the near linearity of this relationship can be used to monitor temperature spectroscopically.

Ratio of Absorption Intensities vs. Temperature

The populations of the single level making up the $^7F_0$ ground state and the two levels comprising the $^7F_1$ state should be describable by the Boltzmann distribution function. The magnitude of the absorption from these three levels, being proportional to their populations, should also be described by such a function. This being the case, the natural logarithm of the ratio of the intensities of the absorption from two of the levels should be proportional to the reciprocal of the absolute temperature $[\ln(A_1/A_2) + \ln(g_2/g_1) \propto (E_2\text{-}E_1)/K * 1/T]$, if the energy difference between the levels remains constant (the temperature effect on this energy difference is on the order of 1.5 cm^{-1}/100 K). The variable g_n is the degeneracy of the nth electronic level and is constant. In Figure 4a are plotted the natural logarithm of the ratio of absorption intensities of some of the transitions arising from levels of the $^7F_0$ and $^7F_1$ states [ln(Integrated Intensity of $^7F_0 \rightarrow {}^5D_3$ transition/Integrated Intensity of $^7F_1 \rightarrow {}^5D_3$ transition)] versus the reciprocal absolute temperature ($1/T\ K^{-1}$). At temperatures up to about 350 K (77 °C), the data remain approximately linear. However, above that temperature, the data appear to show an exponential deviation from the linearity exhibited at lower temperature.

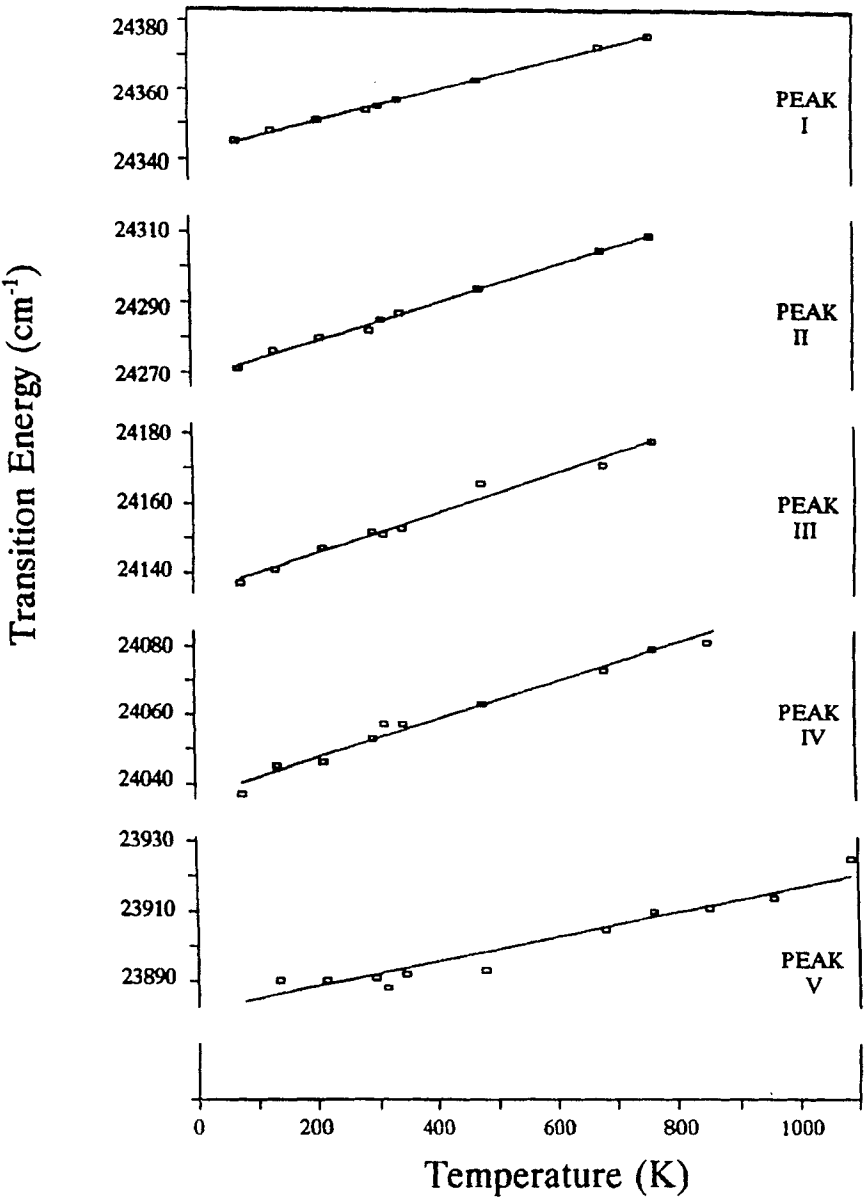

FIG 3. Plot of Absorption Transition Energy (Peaks I-V as Defined in Figure 2) Versus Temperature (K).

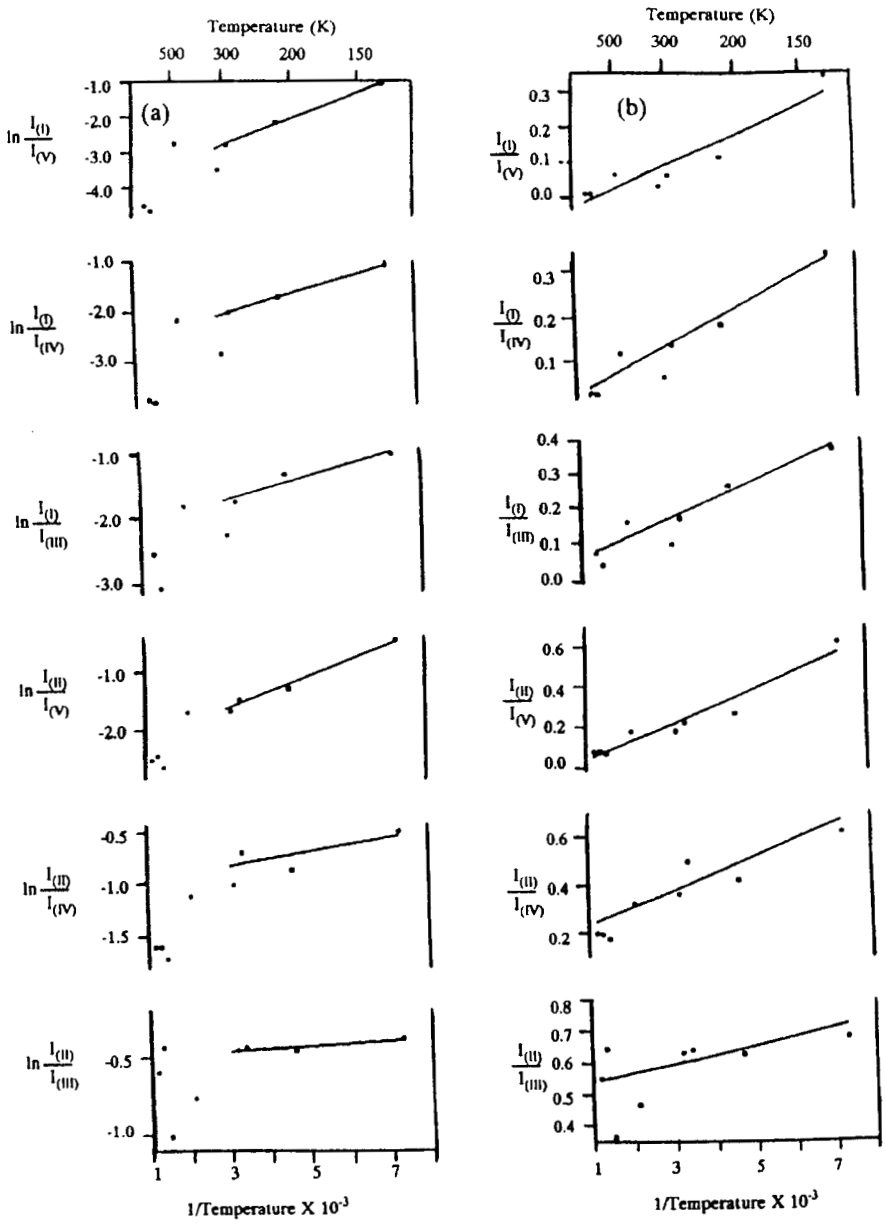

FIG 4. (a) Plot of ln(Intensity Ratio) Versus 1/Temperature (K^{-1}) and (b) Plot of Intensity Ratio Versus 1/Temperature (K^{-1}).

This lack of linearity at higher temperatures may be related to the energy difference between the two levels in question. In such an exponential function as that derived above from the Boltzmann distribution, a small difference in the energies of the two levels should facilitate measurements at low temperatures, while a large difference should yield better results at higher temperatures. Such a sensitivity has been seen in the case of a diamond temperature probe,[2] which has an energy difference on the order of 1300 cm^{-1} between the energy levels involved and yielded better results at higher, rather than lower, temperatures (800 to 1200 K).[2] In the present case, the energy difference is only between 250 and 400 cm^{-1} (depending upon the $^7F_1$ level employed), and the linearity of a plot of the ln(intensity ratio) versus 1/temperature is maintained only to 350 K.

The lack of linearity above 350 K greatly limits the usefulness of this method as a spectral probe of temperature. However, since the deviation appears to be exponential, a similar plot of the absorption intensity ratio (rather than the natural logarithm of the ratio) versus the reciprocal absolute temperature may yield more useful results. Such plots are shown in Figure 4b, where it can be seen that the linearity of the relationship is greatly improved over that seen in Figure 4a. No simple explanation for this enhanced linearity is readily apparent. Neither case exhibits the degree of linearity observed in the plot of transition energy versus temperature (see Figure 3).

CONCLUSIONS

At least two linear relationships between temperature and measured spectral properties of EuOCl have been identified. All absorption transitions exhibit linear shifts to higher energies with increasing temperature. Also a ratio of the absorption intensities of the transitions can be linearly related to the reciprocal of the absolute temperature. The first of these relationships can be used when EuOCl is employed as a spectral monitor of temperature. The second, while exhibiting a linear relationship, cannot be reliably employed in such a method.

ACKNOWLEDGMENTS

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under grant DE-FG05-88ER13865 to the University of Tennessee, Knoxville and contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. Stump NA., Dai S., Del Cul GD., Peterson JR. Absorption Spectrum From Europium Ions in Europium Oxychloride, EuOCl. **Spectrosc. Lett.** 1992; **25**: 1003-1010.

2. Dai S., Young JP., Begun GM., Mamantov G. Temperature Measurement by Observation of the Raman Spectrum of Diamond. **Appl. Spectrosc.** 1992; **46**: 375-377.

3. Mao HK., Bell PM., Shaner JW., Steinberg DJ. Specific Volume Measurements of Cu, Mo, Pd, and Ag and Calibration of the Ruby R_1 Fluorescence Pressure Gauge from 0.06 to 1 Mbar. **J. Appl. Phys.** 1978; **49**: 3276-3283.

4. Cates MR., Allison SW., Franks LA., Borella HM., Marshall BR., Noel BW. Laser-Induced Fluorescence of Europium-Doped Yttrium Oxide for Remote High-Temperature Thermometry. **LIA 1985, Proceedings of the International Congress of Applications of Lasers and Electro Optics** 1985; **49, 51, and 52**: 142-147.

5. Wendlandt WW. The Thermal Decomposition of the Heavier Rare Earth Metal Chloride Hydrates. **J. Inorg. Nucl. Chem.** 1959; **9**: 136-139.

6. Hase Y., Dunstan PO., Temperini MLA. Raman Active Normal Vibrations of Lanthanide Oxychlorides. **Spectrochim. Acta** 1981; **37A**: 597-599.

7. Del Cul GD., Murray GM., Nave SE., Chang CTP., Begun GM., Peterson JR. Luminescence, Absorbance, and Raman Studies of Europium Oxychloride at Various Pressures. **Eur. J. Solid State Inorg. Chem.** 1991; **28**: 155-158.

8. Dai S., Young JP., Begun GM., Coffield JE., Mamantov G. Measurement of Molten Salt Raman Spectra by the Use of Fiber Optics. **Mikrochim. Acta** 1992; **108**: 261-264.

9. Dai S., Mamantov G., Young JP. Measurement of Low Temperature Raman Spectra by Fiber Optics. in preparation.

10. Dieke GH. *Spectra and Energy Levels of Rare Earth Ions in Crystals*, New York: Interscience Publishers, 1968: 349.

Date Received: December 22, 1992

Date Accepted: January 28, 1993