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An extended x-ray absorption fine structure study of rare-earth phosphate glasses near the metaphosphate composition

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A variable-temperature (79, 145, and 293 K) extended x-ray absorption fine structure study, using rare-earth L_{III} absorption edges, is reported for phosphate glasses doped with rare-earth elements (R, where R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er) with compositions close to metaphosphate, $R(PO_3)_3$. The results yield nearest-neighbor R–O distances that demonstrate the lanthanide contraction in a glassy matrix and an R–O coordination intermediate between 6 and 7 for rare-earth ions with smaller atomic number (Z) and 6 for rare-earth ions with larger Z. Thermal parameters show no significant changes in R–O distances or coordination numbers between 293 and 79 K. There is evidence of an R–P correlation between 3.3 and 3.6 Å and the beginning of a second R–O correlation at approximately 4 Å. No R–R correlations up to a distance of approximately 4 Å were observed.

I. INTRODUCTION

Rare-earth-doped phosphate glasses with compositions close to metaphosphate $R(PO_3)_3$ contain very large concentrations of rare-earth ions and as a consequence exhibit novel and useful magnetic and magneto-optical properties. The structural disorder, characteristic of amorphous materials, results in the universal feature of a wide distribution of low-energy excitations that dominate their thermal and optical properties. Recently, this characteristic feature of the glassy state has been extended to magnetic states.^{1,2} Measurements of the low-temperature specific heat and low-frequency Raman scattering have demonstrated the existence of large magnetic contributions to rare-earth metaphosphate glasses. In the case of the Pr glass, multiple splitting of electronic transitions between 4f levels due to topological disorder produces a wide spectrum of low-lying magnetic excitations. The

magnetic contributions to the low-temperature specific heat and low-frequency Raman scattering of the Gd and Sm glasses are quite different in kind from those found for the Pr glass. Understanding the plethora of diverse and unusual properties shown by these magnetic glasses requires knowledge of their structures on the atomic scale, especially of the local environment of the rare-earth ion. Extended x-ray absorption fine structure (EXAFS) is an ideal method for obtaining short-range structural information.

The rare-earth metaphosphate glasses have anomalous thermal, acoustic, and optical properties at low temperatures. Samarium and europium metaphosphate glass show pronounced long-wavelength acoustic mode softening with decreasing temperature or increasing pressure.^{3,4} Analysis of the fluorescence spectrum of europium metaphosphate glass at low temperatures suggests the rare-earth ion may be sited in two possible low-symmetry environments.³ It needs to be established whether the anomalous properties might, in part at least, be attributable to change in the microscopic structure of the glasses with temperature. Rare-earth phosphate glasses exhibit negative thermal expansion at low temperatures.⁵ Although this effect is more pronounced in

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samarium-modified glass, which shows acoustic mode softening, it is also present in that containing lanthanum, which shows normal acoustic mode behavior, namely elastic stiffness increasing with temperature and pressure. A negative contribution to the thermal expansion of metaphosphate glasses has been attributed to the anharmonicity of the excess low-energy vibrational states synonymous with the soft potential model,⁶⁻⁸ and, hence, is expected to be universal to all glasses. The thermal expansion provides a macroscopic approach to exploration of the behavior of the glasses with temperature; it would be instructive to compare its results with the microscopic structural information recorded using EXAFS.

Previous x-ray diffraction studies¹⁰ have shown that the structure of rare-earth metaphosphate glasses is based on a 3-D network of corner linked PO₄ tetrahedra, with the trivalent rare earth ions, R³⁺, occupying sites within the PO₄ skeleton. Complementary EXAFS studies^{9,11,12} showed that each rare-earth ion is surrounded by a nearest-neighbor shell of oxygen atoms at an average R-O distance of 2.25–2.40 Å and that the coordination is in the range 6–10. The lanthanide contraction (a reduction in the rare-earth-ion size with increasing atomic number) was apparent in the changing R-O distance. Further shells were determined, containing phosphorus and oxygen atoms, between 3.3 and 0.36 Å,¹² and at ~4 Å, respectively. These observations are consistent with the rare-earth-ion environment in glasses being similar to that in rare-earth metaphosphate crystals.¹³⁻¹⁵ In these crystals, each rare-earth ion is coordinated to non-bridging oxygen atoms from the phosphate network, and the coordination number varies from 6 to 8 depending on the size of the rare-earth ion.

The previous structural studies of rare-earth metaphosphate glasses have been at ambient temperature. The need for information on which to base interpretations of the temperature-dependent properties of glasses has provided the stimulus for the present EXAFS investigation at lower temperatures. To obtain the local structure around the rare-earth ion, an EXAFS study using the rare-earth L_{III} absorption edges was undertaken. Measurements were made at room temperature (293 K), 145 K, and 79 K. Recently, we have presented results of the initial part of this work, for four rare-earth ions.¹² In this paper, we extend the investigation to include a total sequence of 11 different lanthanide ions: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er.

II. METHOD

A. Experimental

Samples studied contained the rare-earth atoms La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er. Rare-earth phosphate glasses at or near the metaphosphate composition, i.e. (R₂O₃)_x(P₂O₅)_{1-x}, where $x \approx 0.25\%$, were pro-

duced from high-purity (99.9%) grades of 25 mol% rare-earth oxide (R₂O₃) and excess phosphorus pentoxide (P₂O₅), following a method outlined by Mierzejewski *et al.*¹⁶ The preweighed oxides were mixed in an alumina crucible, which was processed through a series of three electric muffle furnaces in which the temperature was progressively increased, reaching a maximum of approximately 1600 °C (the melting temperature depends on the rare-earth oxide). The resulting melt was poured into a split steel mould, preheated to 500 °C, and then annealed at this temperature for 24 h before being cooled slowly at a rate of 0.5 °C/min. The compositions of the glasses, given in Table I, were determined using an electron probe microanalyzer fitted with wavelength dispersive spectrometer, using LaP₅O₁₄, Ce coil, PrP₅O₁₄, NdAl₂, SmS, EuS, GdAl₂, Tb₃Fe₅O₁₂, Dy₃F, Ho₃F, and Er₃F as standards.

The EXAFS experiments were performed on stations 7.1 and 8.1 of the Synchrotron Radiation Source (SRS), at the Daresbury Laboratory, Warrington, U.K.: Station 7.1 uses a double-crystal Si(111) monochromator and station 8.1 uses either a Si(111) or a Si(220) double-crystal monochromator. These monochromators have an energy resolution of 1–3 eV. Harmonic rejection was set at 50% for these experiments. EXAFS spectra were recorded using standard transmission mode with standard ion chamber detectors. To calibrate the energy, 5-μm-thick Cr, Fe, Co, and Ni foils were used, each of which have a K edge at an energy similar to that of the L_{III} edge of the rare-earth element being studied.

For EXAFS measurements the glass samples were powdered and then dusted onto layers of adhesive tape. Typically three layers were used to achieve uniformity across the beam and an absorption edge step corresponding to a change in absorbance, μt, of between 0.5 and 1.5. Data at room temperature, 293 K, were collected with the samples mounted directly in the x-ray beam path. A cryostat was used for the experiments at 145 and 79 K. A spectrum collected for crystalline Nd ultraphosphate NdP₅O₁₄¹³ at 105 K was used to calibrate the data analy-

TABLE I. Compositions of glasses studied.

| Rare earth | Atomic no. | Final rare-earth oxide content (mol%) (±0.005) |
|------------|------------|--|
| La | 57 | (La ₂ O ₃) _{0.1999} (Gd ₂ O ₃) _{0.0001} (P ₂ O ₅) _{0.8000} |
| Ce | 58 | (Ce ₂ O ₃) _{0.235} (P ₂ O ₅) _{0.765} |
| Pr | 59 | (Pr ₂ O ₃) _{0.254} (P ₂ O ₅) _{0.746} |
| Nd | 60 | (Nd ₂ O ₃) _{0.187} (P ₂ O ₅) _{0.813} |
| Sm | 62 | (Sm ₂ O ₃) _{0.195} (P ₂ O ₅) _{0.805} |
| Eu | 63 | (Eu ₂ O ₃) _{0.218} (P ₂ O ₅) _{0.782} |
| Gd | 64 | (Gd ₂ O ₃) _{0.229} (P ₂ O ₅) _{0.771} |
| Tb | 65 | (Tb ₂ O ₃) _{0.263} (P ₂ O ₅) _{0.737} |
| Dy | 66 | (Dy ₂ O ₃) _{0.225} (P ₂ O ₅) _{0.775} |
| Ho | 67 | (Ho ₂ O ₃) _{0.231} (P ₂ O ₅) _{0.769} |
| Er | 68 | (Er ₂ O ₃) _{0.239} (P ₂ O ₅) _{0.761} |

sis parameters used for the glasses. The rare-earth ion in this crystal has a well-defined environment, which is broadly similar to that of the glasses. The crystal sample was prepared in the same manner as the glass samples and, hence, was polycrystalline and isotropic.

B. Data analysis

Data analysis was carried out using the suite of programs at the Daresbury Laboratory.¹⁷ EXCALIB was used to normalize the transmitted x-ray intensity, I_t , to the incident x-ray intensity, I_0 , and hence to obtain absorbance $\mu t = \ln(I_0/I_t)$. EXBACK was used to identify the beginning of the absorption edge, E_0 , to fit pre-edge and post-edge backgrounds, μt_{pre} and μt_{post} , respectively (using standard routines), and hence to obtain the normalized absorbance $\chi(k) = (\mu t(k) - \mu t_{\text{pre}}(k))/(\mu t_{\text{post}}(k) - \mu t_{\text{pre}}(k))$. The final stage of data processing was to extract structural information by using EXCURV92 to model the experimental $\chi(k)$.

The structural information in $\chi(k)$ is clear from the plane wave approximation¹⁸

$$\chi(k) = \sum_i (N_i/kR_i^2) |f_i(k, \pi)| \sin(2kR_i + 2\delta(k) + \varphi_i(k)) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \quad (1)$$

where k is the modulus of the wave vector of the photoelectron, and R_i , N_i , and $2\sigma_i^2$ are the distance, coordination number, and Debye-Waller term (due to static and vibrational disorder) for the i th shell of neighboring atoms. Note that the wave-vector dependence of the scattering differs from that in diffraction by a factor of 2. The additional parameters in Eq. (1) are the backscattering amplitude $f(k, \pi)$, with phase shift $\varphi_i(k)$, the phase shift due to the absorbing atom potential $2\delta(k)$, and the mean free path for inelastic scattering $\lambda(k)$. In earlier EXAFS work these parameters were obtained by measurements on samples of known structure, but now they can be obtained from calculations using atomic potentials.¹⁹ The EXCURV92 program uses fast curved wave theory²⁰⁻²² which alters Eq. (1) by making $f_i(k, \pi)$ dependent on R_i . It is also necessary to include a factor $S_0(k)^2$ which describes the reduction in amplitude due to many-body effects.^{19,20} The k -range of the fits, limited by the presence of the L_{II} edge, covered approximately 2–12 \AA^{-1} , which corresponds to 4–24 \AA^{-1} in conventional diffraction. Equation (1) involves the assumption of a Gaussian distribution for the i th shell of neighboring atoms. However, the effective neighboring atom distribution is slightly asymmetric because of the term $\exp(-2R_i/\lambda(k))$. This means that the fitted distances R_i are shorter than the actual mean distances by an amount $(2\sigma_i^2/R_i)(1 + R_i/\lambda)$, but this term is usually small and hence neglected.²³

A further approximation in Eq. (1) is the assumption of single scattering of the photoelectron. This approxima-

tion has been shown to be reasonable for large values of k . However, multiple scattering can be significant, i.e. up to 10% of single scattering, for values of k up to 7 \AA^{-1} depending on the structure.^{24,25} The effect of multiple scattering can be included by adding terms to the sum over i for each significant multiple scattering path, involving the effective distance, coordination number, and Debye-Waller term [and appropriate values of $|f(k, \pi)|$ and $\varphi(k)$]. The significant multiple scattering paths are generally those involving triangles of nearest-neighbor atoms or forward scattering, which can be expected to have effective distances of approximately $1.5R_1$ and $2R_1$. Hence it is reasonable to neglect multiple scattering effects in the analysis of the nearest-neighbor shell. However, fits to shells beyond the first must be interpreted with caution.

The data for crystalline $\text{NdP}_5\text{O}_{14}$ were used to check that the backscattering and phase shifts calculated by EXCURV92 were acceptable. The values for R_i , N_i , and A_i were fixed to correspond to those in the known crystal structure. A two-shell model was used with four oxygen atoms at 2.40 \AA and four oxygen atoms at 2.48 \AA from the central neodymium atom, and $2\sigma^2$ equal to 0.010 \AA^2 for each shell (typical for crystalline materials). A good fit was obtained with only two adjustable parameters, EF and AFAC. The parameter EF is a correction to the value of E_0 (which approximately corresponds to $k = 0$). In all fitting, EF was allowed to vary, and values obtained were between -10 and -15 eV. The parameter AFAC is a k -independent correction to the EXAFS amplitude, which can include some of the effects of $S_0(k)^2$ and of non-uniformity in sample thickness.²⁶ The value of AFAC was determined to be 0.7 from the fitting of the data for crystalline $\text{NdP}_5\text{O}_{14}$, as described in previous work,¹¹ and this value was fixed for all fitting of the data for glass samples. This is reasonable because the crystal and glass structures are broadly similar at the near-neighbor level and the preparation of all EXAFS samples was identical.

An anomalous feature in the spectra for La, Ce, Pr, and Nd metaphosphate samples occurred between $k = 5.5$ and 6.5 \AA^{-1} ; this is ascribed to double-electron excitations, as seen in previous EXAFS studies of rare-earth-doped silica gels²⁷ and rare-earth metaphosphate glasses.^{11,12} This feature produces peaks at low r values in the Fourier transform of the EXAFS data which may interfere with the fitting of the first neighboring atom shell. This happened in the case of La, for which anomalously small values of the nearest-neighbor R-O distance were obtained. The Fourier filtering method was used to obtain this distance from the La data. In addition, a few spectra showed anomalous features due to known and reproducible imperfections in the monochromator crystal,²⁸ and these were removed by deleting the data points concerned.

An example of the data analysis is given for the Nd metaphosphate glass at 79 K. The background corrected EXAFS spectrum is given in Fig. 1 and also shown is an anomalous feature that was removed before the fitting procedure in EXCURV92 (dotted line on the curve in Fig. 1). The associated Fourier transform of the EXAFS spectrum is given in Fig. 2. The statistical errors in the fit parameters are found from the correlation maps of the pairs of parameters: N_p , A_i and R_p , EF. An example of such a correlation map is shown in Fig. 3 for the parameters N_1 and A_1 . The bold contour represents the 95% confidence interval around the least sum of squares

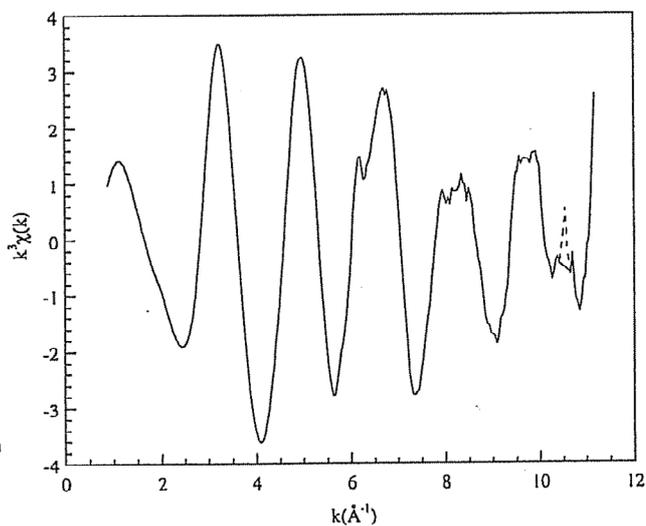


FIG. 1. EXAFS $k^3\chi(k)$ for neodymium phosphate glass $(Nd_2O_3)_{0.187}(P_2O_5)_{0.813}$ at 79 K. The data used in the analysis are shown (solid line) and also an anomalous feature that was removed from the data (dotted line).

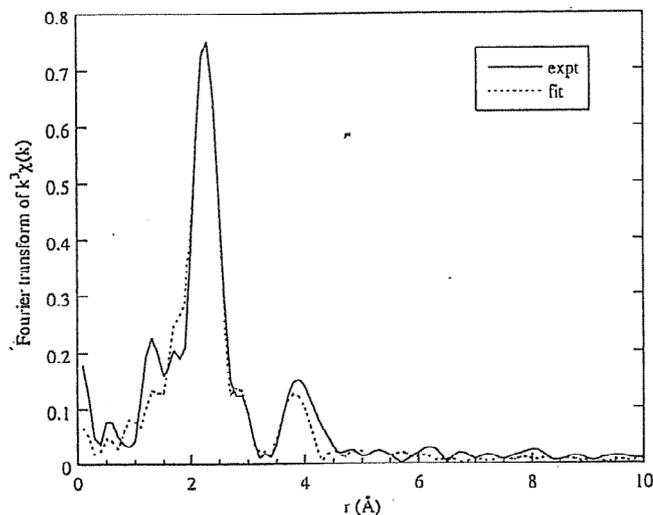


FIG. 2. Fourier transform of $k^3\chi(k)$ as a function of distance (\AA) for neodymium phosphate glass $(Nd_2O_3)_{0.187}(P_2O_5)_{0.813}$ at 79 K.

(marked by a cross on the plot), and it is from the projection of this ellipse on the relevant axes that the statistical errors were obtained.

III. RESULTS

The experimental data and the theoretical best fits for all of the samples at 145 K are shown in Fig. 4. The corresponding residual R values where¹⁷

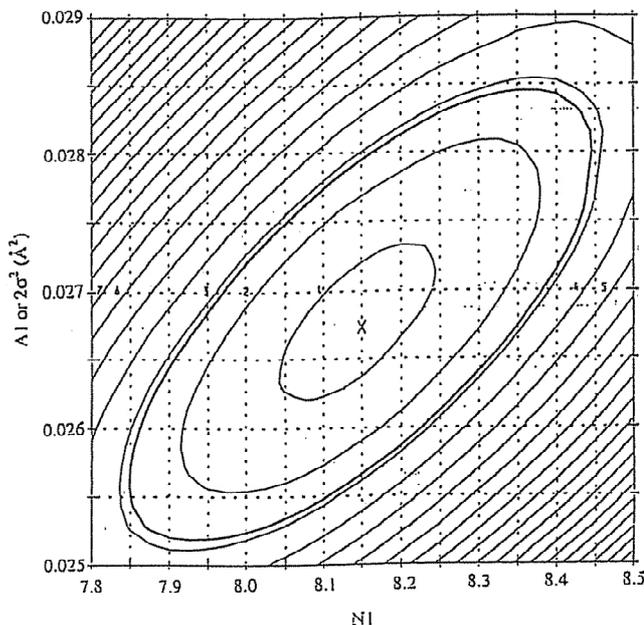


FIG. 3. Correlation map for neodymium phosphate glass $(Nd_2O_3)_{0.187}(P_2O_5)_{0.813}$ at 79 K showing the goodness of fit for the parameters N_1 (number of neighboring oxygen atoms in the first shell) and A_1 (Debye-Waller factor, $2\sigma^2$, for the first shell).

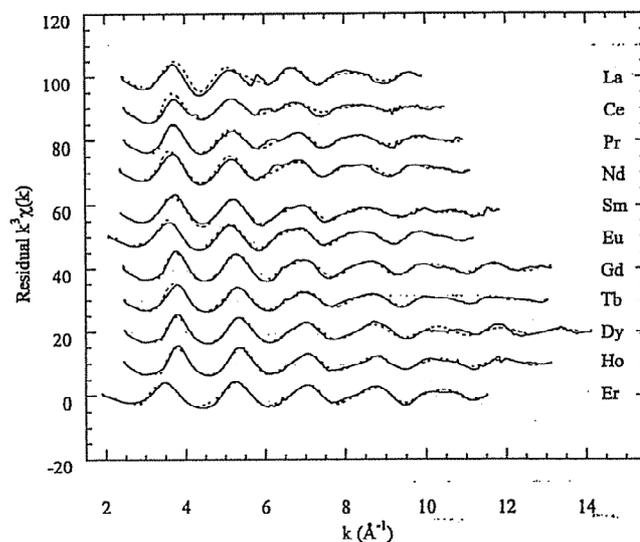


FIG. 4. La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er metaphosphate glass EXAFS $k^3\chi(k)$, experimental data (solid lines) and theoretical fit (dotted lines).

$$R = \sum_i \left(\frac{1}{\sigma(i)} \right) (|\text{expt}(i) - \text{theory}(i)|) \times 100\% ,$$

$$\left(\frac{1}{\sigma(i)} \right) = k(i)^3 / \sum_j (k(j)^3 |\text{expt}(j)|) ,$$

are given for all temperatures in Table II. These values indicate how well the theoretical fit matches the experimental data; for a perfect match, $R = 0$, and for EXAFS measurements, results where $R \leq 25$ are considered to be good. The results from the fitting of the EXAFS spectra are shown in Tables III and IV. The first shell around the rare-earth ion for all of the glasses was found to contain oxygen atoms. The variation of the R-O distance, R_{RO} , with atomic number of the rare-earth ion Z , is shown in Fig. 5(a). The decrease in R_{RO} with increasing Z clearly demonstrates the lanthanide contraction. The values obtained for R_{RO} compare well with those calculated from the tables of ionic radii,²⁹ assuming a valence of 3+ and a coordination number of 6 for all of the rare-earth elements studied here. The comparison is less good for cal-

culated values corresponding to a coordination number of 7 (long dashed line), with the exception of results for the La, Ce, and Pr glasses. The comparison is poor for calculated values corresponding to a coordination number of 8 (short dashed line).

The first shell coordination numbers of the oxygen atoms around the rare earth, N_{RO} , are shown in Fig. 5(b). N_{RO} is found to vary between 5 and 8. This is slightly lower than the range of 6 to 10 found by Bowron *et al.*^{9,11} The values of N_{RO} are not entirely consistent with the values of R_{RO} , and this may be due to the lower precision of the former compared with the latter.

A second shell fit was obtained, corresponding to an R-P correlation, with distances of between 3.3 and 3.6 Å, except for the Ce, Tb, Dy, and Er phosphate glasses. These distances are reported in Table IV. The associated errors given here were calculated according to the aforementioned statistical model. However, this model does not take into account effects such as multiple scattering or the possible presence of other underlying correlations that complicate such spectra at these distances. Therefore, we expect the true errors of these distances to be rather larger than those tabulated. The distances obtained are consistent with the distance expected from the crystalline analogues of the metaphosphate glasses.¹³⁻¹⁵ The coordination numbers have relatively large errors, as tends to be the case for EXAFS-determined coordination numbers of shells further away from the central excited atom, and so have not been included in Table IV. A third shell fit was also obtained, corresponding to a second R-O correlation at a distance of approximately 4 Å, except for the La and Ce phosphate glasses. These distances are reported in Table IV. For the same reasons as those detailed for the R-P distances, the associated errors reported here are likely to be significantly underestimated. The coordination numbers for this shell were also subject to large errors and so have not been included in Table IV. No R-R correlations were found within the limits of the data, up to -4 Å.

TABLE II. Residual (R) values for each rare-earth phosphate glass EXAFS spectrum reported herein.

| Glass modifier | R | | |
|----------------|--------------------|---------------------|---------------------|
| | $T = 79 \text{ K}$ | $T = 145 \text{ K}$ | $T = 293 \text{ K}$ |
| La | 31.0 | 31.2 | 34.2 |
| Ce | 26.9 | 29.5 | 26.4 |
| Pr | 14.8 | 14.1 | 14.5 |
| Nd | 16.1 | 20.8 | 16.0 |
| Sm | 25.0 | 19.1 | 16.6 |
| Eu... | 16.2 | 18.1 | 18.5 |
| Gd | 16.4 | 17.8 | 20.6 |
| Tb | 18.5 | 19.5 | 12.7 |
| Dy | 38.8 | 23.6 | 20.0 |
| Ho | 20.4 | 19.2 | 20.2 |
| Er | 20.5 | 20.7 | 18.1 |

TABLE III. Summary of first-shell information obtained from EXAFS spectra for the rare-earth phosphate glasses in the vicinity of the metaphosphate composition, where R represents the rare-earth ion. The results marked with an asterisk were obtained by using Fourier filtering.

| Glass modifier | N_{RO} | | | R_{RO} | | | $2\sigma^2 (\text{Å}^2) (\text{R-O})$ | | |
|----------------|--------------------|---------------------|---------------------|--------------------|---------------------|---------------------|---------------------------------------|---------------------|---------------------|
| | $T = 79 \text{ K}$ | $T = 145 \text{ K}$ | $T = 293 \text{ K}$ | $T = 79 \text{ K}$ | $T = 145 \text{ K}$ | $T = 293 \text{ K}$ | $T = 79 \text{ K}$ | $T = 145 \text{ K}$ | $T = 293 \text{ K}$ |
| La | 5.9 ± 0.4 | 6.0 ± 0.6 | 7.3 ± 1.2 | *2.41 ± 0.02 | *2.42 ± 0.02 | *2.42 ± 0.03 | 0.013 ± 0.004 | 0.017 ± 0.005 | 0.030 ± 0.012 |
| Ce | 4.8 ± 0.5 | 6.2 ± 1.8 | 4.8 ± 0.5 | 2.38 ± 0.01 | 2.39 ± 0.03 | 2.35 ± 0.01 | 0.006 ± 0.003 | 0.023 ± 0.013 | 0.013 ± 0.004 |
| Pr | 6.3 ± 0.3 | 6.3 ± 0.2 | 6.7 ± 0.3 | 2.369 ± 0.007 | 2.367 ± 0.008 | 2.367 ± 0.007 | 0.017 ± 0.002 | 0.017 ± 0.013 | 0.022 ± 0.003 |
| Nd | 8.1 ± 0.3 | 7.7 ± 0.4 | 8.6 ± 0.3 | 2.34 ± 0.01 | 2.33 ± 0.01 | 2.34 ± 0.01 | 0.027 ± 0.002 | 0.021 ± 0.003 | 0.037 ± 0.001 |
| Sm | 6.9 ± 0.9 | 6.4 ± 0.3 | 6.9 ± 0.3 | 2.32 ± 0.01 | 2.33 ± 0.01 | 2.31 ± 0.01 | 0.013 ± 0.005 | 0.016 ± 0.002 | 0.019 ± 0.002 |
| Eu | 6.0 ± 0.3 | 6.0 ± 0.3 | 6.2 ± 0.3 | 2.30 ± 0.01 | 2.32 ± 0.01 | 2.31 ± 0.01 | 0.012 ± 0.002 | 0.012 ± 0.002 | 0.016 ± 0.002 |
| Gd | 6.1 ± 0.3 | 6.0 ± 0.2 | 6.5 ± 0.4 | 2.297 ± 0.001 | 2.29 ± 0.01 | 2.285 ± 0.005 | 0.009 ± 0.001 | 0.011 ± 0.001 | 0.014 ± 0.002 |
| Tb | 5.3 ± 0.2 | 5.5 ± 0.2 | 5.8 ± 0.2 | 2.25 ± 0.01 | 2.25 ± 0.01 | 2.267 ± 0.005 | 0.012 ± 0.001 | 0.013 ± 0.002 | 0.016 ± 0.001 |
| Dy | 5.5 ± 0.5 | 5.8 ± 0.4 | 5.5 ± 0.3 | 2.25 ± 0.01 | 2.25 ± 0.01 | 2.22 ± 0.01 | 0.011 ± 0.002 | 0.011 ± 0.003 | 0.014 ± 0.002 |
| Ho | 5.6 ± 0.3 | 6.0 ± 0.3 | 5.8 ± 0.4 | 2.232 ± 0.006 | 2.236 ± 0.008 | 2.228 ± 0.002 | 0.010 ± 0.002 | 0.012 ± 0.001 | 0.012 ± 0.002 |
| Er | 5.7 ± 0.4 | 5.7 ± 0.3 | 5.7 ± 0.4 | 2.224 ± 0.005 | 2.224 ± 0.006 | 2.225 ± 0.005 | 0.010 ± 0.002 | 0.009 ± 0.002 | 0.010 ± 0.002 |

TABLE IV. Summary of second- and third-shell information obtained from EXAFS spectra for the rare-earth phosphate glasses in the vicinity of the metaphosphate composition, where R represents the rare-earth ion. The results marked with an asterisk were obtained by using Fourier filtering.

| Glass modifier | R-P correlation | | | Second R-O correlation | | |
|----------------|-------------------|-------------------|-------------------|------------------------|-----------------|-----------------|
| | $T = 79$ K | $T = 145$ K | $T = 293$ K | $T = 79$ K | $T = 145$ K | $T = 293$ K |
| La | * 3.61 ± 0.04 | * 3.60 ± 0.03 | * 3.54 ± 0.04 | ... | ... | ... |
| Ce | ... | ... | ... | ... | ... | ... |
| Pr | 3.39 ± 0.04 | 3.40 ± 0.04 | 3.40 ± 0.04 | 4.13 ± 0.02 | 4.13 ± 0.02 | 4.13 ± 0.02 |
| Nd | 3.42 ± 0.03 | 3.41 ± 0.04 | 3.44 ± 0.03 | 4.07 ± 0.02 | 4.08 ± 0.02 | 4.08 ± 0.02 |
| Sm | 3.42 ± 0.05 | 3.41 ± 0.05 | 3.40 ± 0.02 | 4.08 ± 0.01 | 4.07 ± 0.02 | 4.03 ± 0.01 |
| Eu | 3.34 ± 0.05 | 3.33 ± 0.05 | 3.34 ± 0.05 | 4.04 ± 0.02 | 4.03 ± 0.02 | 4.07 ± 0.02 |
| Gd | 3.17 ± 0.03 | 3.21 ± 0.15 | 3.18 ± 0.06 | 4.01 ± 0.02 | 4.01 ± 0.02 | 4.01 ± 0.03 |
| Tb | ... | ... | ... | 3.95 ± 0.01 | 3.94 ± 0.02 | 4.01 ± 0.01 |
| Dy | ... | ... | ... | 3.94 ± 0.04 | 3.98 ± 0.02 | 3.92 ± 0.02 |
| Ho | 3.15 ± 0.07 | 3.11 ± 0.07 | 3.12 ± 0.06 | 3.96 ± 0.02 | 3.98 ± 0.02 | 3.95 ± 0.03 |
| Er | ... | ... | ... | 3.95 ± 0.02 | 3.95 ± 0.02 | 3.97 ± 0.02 |

The Debye-Waller terms for the first shell, $A_{RO} = 2\sigma_{RO}^2$ are shown in Fig. 5(c). The values of A_{RO} are expected to decrease with decreasing temperature. The results show this within experimental error. In order to elucidate the temperature dependence, we have averaged the value of A_{RO} for a given temperature over the different rare earths. The averaging is performed to reduce the statistical error and is not physically meaningful, although it can be considered as a rough estimate of A_{RO} for intermediate values of Z . The average values of A_{RO} obtained for 293, 145, and 79 K, respectively, were 0.019, 0.015, and 0.013 \AA^2 , with a statistical error in the averages of 0.001 \AA^2 . These clearly show the effect of temperature.

IV. DISCUSSION

Figure 5(a) shows that the values of R_{RO} are close to those predicted for 3+ ions with a coordination of 6. This is consistent with 3+ being the preferred valence state for these ions in the metaphosphate glass structure. Distances calculated from tables for ionic radii assuming valences of 2+ and 4+ and coordination numbers of 6, 7, and 8 were in poor agreement with the results [and as a consequence are not illustrated in Fig. 5(a)]. This is in accord with the optical properties: the fluorescence and absorption spectra of Sm (Ref. 30) and Eu (Ref. 3) metaphosphate glasses show features arising solely from trivalent ions. Other valence states, which can occur in certain lanthanides, such as 2+ (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy) or 4+ (Ce, Pr, Tb) or an intermediate valence, are not favored in these glasses.

We now consider whether there is any linear Z dependence of the values of R_{RO} , albeit with a slight discontinuity at gadolinium on account of the half-filled 4f electron shell of the Gd^{3+} ion. Relative to the calculated values of R_{RO} for 3+ ions with constant coordination, the measured values of R_{RO} show an increase as Z decreases.

For rare earths with larger Z , the values of R_{RO} are slightly below those calculated for a coordination of 6. However, we consider an R-O coordination of less than 6 to be unlikely, in view of the overall balance of evidence relating to the coordinations of rare-earth ions. Thus there may be a small systematic error in the values of R_{RO} . One such error is the correction of $(2\sigma^2/R_i)(1 + R_i/\lambda)$ which has been neglected.²³ Applying this factor would increase the values of R by approximately 0.01 \AA , assuming a typical value of 10 \AA for λ (e.g., Ref. 24). For rare-earth with lower Z , the values of R_{RO} are intermediate between those calculated for coordinations of 6 and 7. A coordination of 7 has recently been reported for a La metaphosphate glass by Hoppe *et al.*³¹

The variation in N_{RO} with Z is shown in Fig. 5(b). These values have larger uncertainty than those for R_{RO} . However, we note that they are largely consistent with the values of R_{RO} . That is, N_{RO} increases as Z decreases with values intermediate between 6 and 7 for rare earths with smaller Z and slightly below 6 for rare earths with larger Z . If we consider that a coordination of less than 6 is unlikely, this suggests a possible systematic error in N_{RO} . One such error could be in the value of the fixed parameter AFAC. An increase in AFAC from 0.7 to 0.75 would give values of N_{RO} closer to 6 for rare earths with larger Z . There are two exceptions to the above trends. The value of N_{RO} for the Nd sample is inconsistently large and for the Ce sample is inconsistently small, compared with R_{RO} . Note that the values of the Debye-Waller terms, A_{RO} , for these two samples also seem to be larger and smaller (respectively) than for the other samples. Corrections to the data that improved the values of A_{RO} should also improve the values of N_{RO} because these are correlated parameters. Aside from this, the interpretation based on R_{RO} values is expected to be more reliable, because of the greater precision in this parameter.

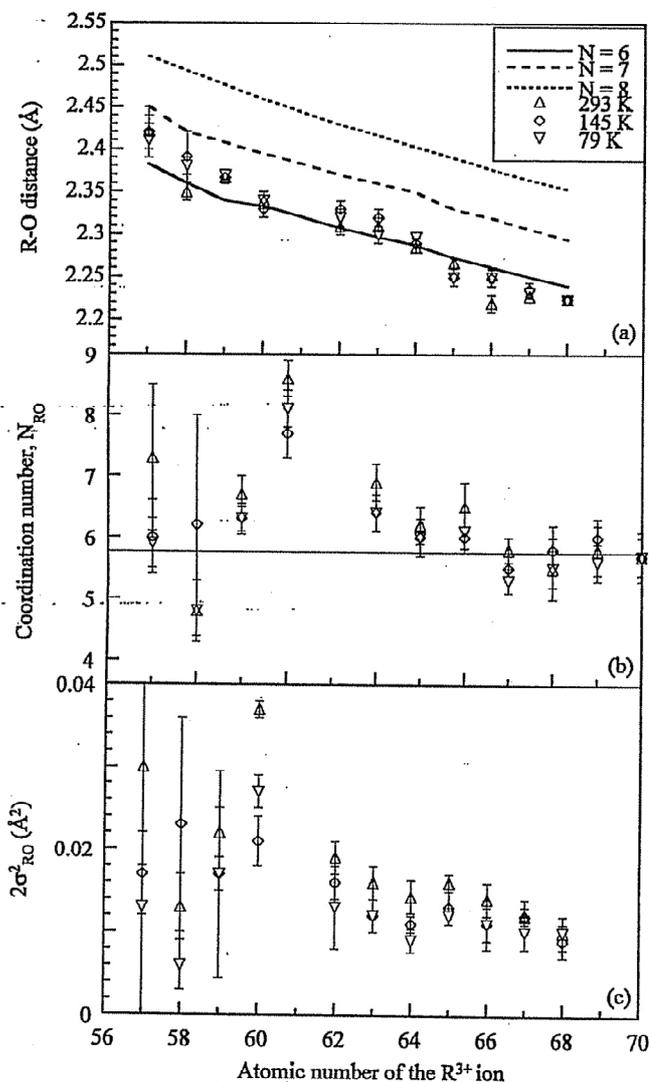


FIG. 5. Variation of (a) R_{RO} (b) N_{RO} , and (c) $2\sigma_{RO}^2$ with the rare-earth-ion atomic number in the glasses at the three temperatures 79, 145, and 293 K. The lines on the plot in part (a) represent the values expected for R-O distance calculated from tables of ionic radii for R^{3+} and for coordination of 6 (solid line), 7 (long dashed line), and 8 (short dashed line). A solid guideline in part (b) is included showing $N_{RO} = 6$ (average of the measured N_{RO} is 6.1).

The observed Z dependence of the R-O structural parameters, R_{RO} and N_{RO} , can be understood in terms of the Z -dependence of rare-earth-ion size. Rare earths with smaller Z have larger radii and are not coordinatively saturated by only 6 oxygens.³² The structures of crystal rare-earth metaphosphates also show a Z -dependence. For rare earths La to Gd the orthorhombic structure is observed, whereas for rare earths Sm to Yb the monoclinic structure is observed.³³ The monoclinic structure has a coordination of 6. The orthorhombic structure has a coordination of 6 but with an additional 2 oxygens at an approximately 15% larger distance, such that the overall coordination can be considered as somewhat greater than

6 (but less than 8). This 6 + 2 type of coordination was observed in a $\text{Eu}(\text{PO}_3)_3$ glass through an x-ray diffraction study.³⁴ The EXAFS results reported here could not confirm the presence of these outer two oxygen atoms although this may be because the boundaries between these two different coordinations encompass the rare earths Sm, Eu, and Gd. These rare earths also fall approximately in the middle of the trends seen for the glasses, in Figs. 5(a) and 5(b).

Another factor which might influence the structure of the glasses is the composition. The ratio of non-bridging oxygen to rare-earth ions increases as the percentage of rare-earth oxide, x , decreases. In the case of divalent metal metaphosphate glasses, Hoppe has argued that this can enable an increased oxygen coordination of cations.³⁵ Furthermore, in crystal rare-earth metaphosphates, with $x = 0.25$, the coordination is 6 or somewhat larger than 6. However, for crystal rare-earth ultraphosphates, with $x = 0.17$, the coordination number is 8 and R_{RO} is equal to the calculated value for a 3+ ion with coordination of 8. To consider the effect of composition, we can consult Table I. This shows that most of the samples are in the region of the metaphosphate composition, with the exception of the La, Nd, and Sm samples which are significantly shifted toward the ultraphosphate composition. However, the results for these samples do not depart from the trends seen for other rare earths. The sole exception is the N_{RO} value of approximately 8 for the Nd sample. Considering the balance of results, and the greater precision in R_{RO} , we find no clear evidence for a composition effect. Further work is in progress to help clarify this matter.

We now consider the mean-square deviation in R-O distances, $\sigma_{RO}^2 = A_{RO}/2$, due to thermal and static disorder. From the values of A_{RO} averaged over different rare earths, the effect of temperature on σ_{RO}^2 is a decrease from approximately 0.0095 \AA^2 at 293 K, to 0.0075 \AA^2 at 145 K, to 0.0065 \AA^2 at 79 K. The linear dependence on T is consistent with the predicted behavior for σ^2 (e.g., Ref. 36). On this basis, the typical contribution due to static disorder can be estimated at 0.006 \AA^2 . This can be compared with estimates of the static disorder in rare-earth metaphosphate crystals: the mean-square deviations of the R_{RO} distances are 0.005 and 0.001 \AA^2 in the orthorhombic Yb and La metaphosphate crystal structures, respectively.

One of the aims of this study was to investigate the possible temperature dependence of the rare-earth environment. Inspection of the values of R_{RO} and N_{RO} in Table III and Figs. 5(a) and 5(b) does not show any clear trend with temperature relative to the uncertainties. To check for subtle trends, we calculated the averages of R_{RO} and N_{RO} for a given temperature over different rare earths. This is not physically meaningful but reduces the effect of statistical error. Between 293 and 79 K, the

average values showed negligible change in R_{RO} and a marginal decrease of approximately 0.3 in N_{RO} . The latter result may be influenced by the relatively large change in A_{RO} , because A_{RO} and N_{RO} are correlated parameters. Thus we consider the assumption of no temperature dependence to be valid for R_{RO} and to be reasonable for N_{RO} . On this basis, we have calculated for each rare earth the averages of R_{RO} and N_{RO} over the three different temperatures, in order to reduce the effect of statistical error. The results, shown in Table V and Fig. 6, confirm the trends already discussed. Furthermore, they suggest that the Z-dependence may be localized to a change occurring between Gd and Tb. As discussed above, the crystal rare-earth metaphosphates exhibit such a Z-dependence.

We now turn our attention to the fits to higher shells. As discussed above, these involve large uncertainties,

TABLE V. Values of R-O distance, R_{RO} , and coordination number, N_{RO} , obtained by averaging over temperatures of 293, 145, and 79 K. These values appear in Fig. 6.

| Glass modifier | R_{RO} (Å) (± 0.01) | N_{RO} ($\pm 10\%$) |
|----------------|--------------------------------|----------------------------|
| La | 2.42 | 6.4 |
| Ce | 2.37 | 5.3 |
| Pr | 2.37 | 6.4 |
| Nd | 2.34 | 8.1 |
| Sm | 2.32 | 6.7 |
| Eu | 2.31 | 6.1 |
| Gd | 2.29 | 6.2 |
| Tb | 2.26 | 5.5 |
| Dy | 2.24 | 5.6 |
| Ho | 2.23 | 5.8 |
| Er | 2.22 | 5.7 |

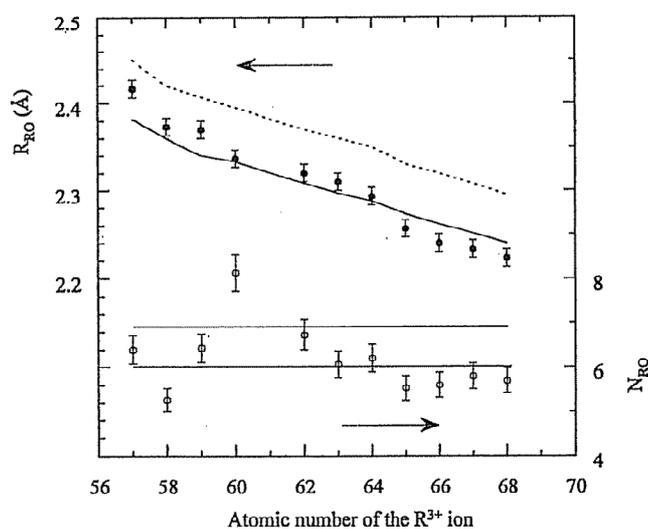


FIG. 6. Variation of R_{RO} and N_{RO} with atomic number of the metaphosphate glasses. The values are obtained from averaging over the results from three different temperatures: 293, 145, and 79 K.

and only the shell distances are reported. For the second shell, the fitted values of R-P coordination, N_{RP} , were between 3 and 7. This is compatible with a predicted coordination of 6 to 7, based on the coordination in rare-earth metaphosphate crystals. (Note that N_{RP} cannot be greater than N_{RO} because each non-bridging oxygen can be bonded to at most one P.) In the metaphosphate crystals, a second R-O correlation extends from approximately 4.0 to 4.5 Å, with a total coordination number approximately 20. The fitted third shell distances were between 3.9 and 4.2 Å. Thus it is possible that the EXAFS results correspond only to the start of the second R-O correlation. It should also be noted that the second and third shells can be expected to contain multiple scattering contributions. Calculations for octahedral NdO_6 clusters shows that triangular and collinear multiple scattering paths makes contributions at distances corresponding to the second and third shells.²⁵ We have carried out preliminary calculations for octahedral ErO_6 clusters that support this. However, these calculations on distances do not include R-P and second R-O correlations which we know will be present in these glasses. Furthermore, disorder in glasses reduces the significance of multiple scattering effects (as seen in amorphous Si).³⁷ Hence, we do not expect the multiple scattering contribution to be dominant.

The absence of R-R correlations within the short range order of the EXAFS spectrum is particularly important when considering the optical properties observed since close R-R distances would result in cross-relaxation of rare-earth energy levels, thereby lowering the extent of population inversion possible in these materials. Moreover, the lack of rare-earth clustering demotes the possibility of a cooperative transition being responsible for the observed magnetic properties. The lower limit of 4 Å observed for R-R correlations can be compared with the feasible range for rare-earth separation of 3.5–6 Å, which is estimated in the following way: for rare-earth ions with octahedral coordination to oxygen, a rare-earth separation of less than approximately 3.5 Å is not possible if there is only corner-sharing of octahedra. Indeed, complementary reverse Monte Carlo simulation results^{31,38} predict an R-R separation within this range (at 4.4 Å) and density considerations mean that it is not possible to separate all rare-earth ions by more than approximately 6 Å.

Anomalous changes observed at low temperatures in the acoustic,^{30,39} thermal,⁸ and optical³ properties of these glasses are not due to observable changes in structure, within the limits of sensitivity of the EXAFS technique used here and the temperature range available. However, there is evidence for a degree of Z-dependence of the structure with some correspondence to that seen for rare-earth metaphosphate crystals. We note that anomalous properties have been reported for glasses with

rare earths of intermediate Z , i.e., Sm, Eu, and Gd. Further studies are currently being carried out using x-ray diffraction to probe the existence of more subtle structural changes at longer distances in these glasses.

V. CONCLUSIONS

The results reported herein demonstrate the lanthanide contraction for the set of trivalent rare-earth ions studied. Each of these ions has a similar local environment to those in the metaphosphate crystals, the ions being coordinated to approximately six non-bridging oxygen atoms. The near-neighbor coordination numbers show a degree of Z -dependence. The results for rare earths with smaller Z are consistent with coordinations intermediate between 6 and 7, whereas the results for rare earths with larger Z are consistent with coordinations of 6. The change between these two types of coordination occurs around Gd. There is no significant temperature dependence of near-neighbor distances or coordination numbers, in the temperature range from 79 to 293 K. This indicates that the anomalous thermal, acoustic, and optical properties of these glasses at low temperature do not result from significant temperature-induced changes in the rare-earth environment. The rare-earth ions in the glasses are separated by distances greater than ~ 4 Å. This can be compared with a lower limit of approximately 3.5 Å, which exists in the case of R-O octahedra which only share corners.

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