

## Reply to "Comment on 'Ruby at high pressure. I. Optical line shifts to 156 GPa'"

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In our paper [Phys. Rev. B **40**, 5724 (1989)] we made independent interpretations based on published data, and did not intend to quote Vohra, Vanderborgh, Desgreniers, and Ruoff. We believe that the fluorescence published as evidence for pressures of 460–550 GPa in diamond-anvil-cell experiments was due to ruby. Therefore, claims of 460 and 550 GPa are acceptable to within the accuracy of extrapolations of the ruby pressure scale.

In our paper<sup>1</sup> we made independent interpretations based on published data, including the work of Vohra, Vanderborgh, Desgreniers, and Ruoff. The manner in which we cited their work may have inadvertently caused the reader to think that our interpretations were theirs also. It is our interpretation that while the "possibility of misinterpreting fluorescence data at ultrahigh pressure"<sup>2</sup> may exist, the ruby fluorescence observed by Xu *et al.*<sup>3</sup> and Moss *et al.*<sup>4</sup> was not misinterpreted, and therefore the claims of 550 GPa (Ref. 3) and 460 GPa (Ref. 4) are valid to the extent that extrapolations of the ruby pressure scale are valid.

In their Comment, Vohra, Vanderborgh, Desgreniers, and Ruoff<sup>2</sup> (subsequently referred to as VVDR) contend that fluorescence peaks identified as ruby and used to claim pressures of 550 GPa (Ref. 3) and 460 GPa (Ref. 4) may have been due to diamond. Based on the spatial and pressure dependences of the diamond fluorescence observed by Vohra *et al.*<sup>5–7</sup> and the fluorescence observed by Xu *et al.*<sup>3</sup> and by Moss *et al.*,<sup>4</sup> we believe that the original identification of the fluorescence of Xu *et al.* and Moss *et al.* as due to ruby was correct. Our statement<sup>1</sup> that "recent results suggest that these fluorescence peaks are due to ruby" was our interpretation of the accumulated data, and was not intended as a quotation of Vohra *et al.*<sup>5–7</sup>

Vohra *et al.*<sup>5</sup> originally questioned the identification of ultrahigh-pressure fluorescence peaks, as ruby, when they observed apparent contradictions in their concurrent pressure measurements using the ruby pressure scale and x-ray-diffraction techniques. Vohra *et al.* presented fluorescence spectra (Fig. 4 of Ref. 5) which showed no significant change across the sample surface at a spatial separation of 75  $\mu\text{m}$ . A comparison of the ambient-pressure diamond-fluorescence data presented by Vohra *et al.*<sup>6</sup> with their high-pressure data<sup>5</sup> suggested to us that their high-pressure fluorescence peaks arose from diamond. The diamond fluorescence reported by Vohra *et al.*<sup>5,6</sup> shows significant variation in the fluorescence intensity of different diamonds, but little evidence for a pressure dependence of the peak positions. The lack of spatial and pressure dependences is inconsistent with the high-pressure fluorescence arising from ruby.

In contrast, the fluorescence peaks observed by Xu *et al.*<sup>3</sup> and Moss *et al.*<sup>4</sup> showed strong spatial and pres-

sure dependences. In the experiments of Moss *et al.*, the fluorescence peaks showed large changes occurring for 2- $\mu\text{m}$  movements across the sample surface. Fluorescence peaks were observed in areas where ruby was present and not observed where ruby was not present. In these experiments and in those of Xu *et al.*,<sup>3</sup> pressure-dependent shifts of 65–80 nm were observed which were consistent with increases in the applied load. In addition, pressure profiles taken across the sample surface<sup>4,8</sup> yielded pressure profiles consistent with those obtained at lower pressures and with finite-element modeling calculations.<sup>4,9,10</sup> Based on these observations, we are confident that the fluorescence peaks observed by Xu *et al.* and by Moss *et al.* were due to ruby and not due to diamond.

VVDR note correctly that the ruby pressure scale has only been calibrated to 180 GPa.<sup>11</sup> We agree<sup>1</sup> that until a ruby calibration is performed, claims of 550 GPa (Ref. 3) and 460 GPa (Ref. 4) should be viewed with appropriate caution. However, we do not feel that "substantial skepticism"<sup>2</sup> is warranted. In our paper<sup>1</sup> we presented an analysis of the present uncertainty in the extrapolation of the ruby pressure scale. We discussed the possible overestimation of pressure due to line crossing if the  $R'_3$  line was misidentified as the  $R_1$  line, as well the possible underestimation of pressure due to effects of nonhydrostaticity.

Evidence that the ruby scale is reasonably well behaved up to the 250-GPa region can be drawn from recent experiments by Hemley and Mao.<sup>12</sup> They have obtained ruby-fluorescence spectra up to 248 GPa in conjunction with Raman data on the hydrogen vibron. The shift of the vibron frequency at ultrahigh pressures determined by extrapolation of the ruby scale is consistent with the vibron shift at lower pressures.

VVDR suggest that the maximum pressure achieved at present may be in the 280–300-GPa range, not the 460–550-GPa range. They base this suggestion on an oversimplified discussion of the relationship between anvil-tip (central flat) size and the maximum achievable pressure, as well as an assumption that x-ray measurements are highly accurate. As shown by Moss *et al.*,<sup>4,9,10</sup> the maximum achievable pressure in a given experiment is a very complex function of diamond shape, gasket properties, and sample properties. Maximum pressure also depends on the selection of anvils, the

design of the supporting apparatus, and the skill of the experimenter in achieving diamond alignment and other critical parameters. In addition, x-ray determinations of pressure in nonhydrostatic materials such as a gasket in diamond-anvil cells generally underestimate pressure. This is due to the fact that an x-ray beam perpendicular to the diamond anvils measures the lattice spacings of the sample only in the low-strain directions normal to the applied stress. In nonhydrostatic ruby calibrations<sup>11,13</sup> this was considered a major source of error.

We believe that ruby-fluorescence peaks have been measured with pressure shifts into the wavelength range above 800 nm (Refs. 3, 4, and 8) giving extrapolated highest pressures of 460 and 550 GPa. Ruoff and Vohra<sup>14</sup> have observed, using our time-resolved technique,<sup>15</sup> ruby fluorescence that peaked at approximately 760 nm, which gives an extrapolated pressure of 250–300 GPa. This supports our contention that ruby fluorescence can be continuously measured to the highest pres-

ures currently achievable in a diamond-anvil cell. The broadening of the ruby lines, noted by VVDR, in nonhydrostatic samples at very high pressure does not rule out reliable use of the ruby pressure scale if the broadening mechanism is well understood and a proper calibration is performed. It is likely that the broadening is largely due to pressure gradients,<sup>1</sup> and so would be much less of a problem in more uniform pressure environments.

We reaffirm our conclusion<sup>1</sup> that pressures based on extrapolations beyond the calibrated range of the ruby scale must be interpreted cautiously, with due consideration of the present uncertainties. With the attainment of ultrahigh pressures becoming more common, an optical pressure scale that allows easy and reliable pressure characterization is needed. Therefore, extension of the ruby calibration to higher pressures, and work dedicated to the understanding of nonhydrostatic ruby fluorescence, are very important.

<sup>1</sup>J. H. Eggert, K. A. Goettel, and I. F. Silvera, *Phys. Rev. B* **40**, 5724 (1989).

<sup>2</sup>Y. K. Vohra, C. A. Vanderborgh, S. Desgreniers, and A. L. Ruoff, preceding paper, *Phys. Rev. B* **42**, 9191 (1990).

<sup>3</sup>J. A. Xu, H. K. Mao, and P. M. Bell, *Science* **232**, 1404 (1986).

<sup>4</sup>W. C. Moss, J. O. Hallquist, R. Reichlin, K. A. Goettel, and S. Martin, *Appl. Phys. Lett.* **48**, 1258 (1986).

<sup>5</sup>Y. K. Vohra, S. J. Duclos, K. E. Brister, and A. L. Ruoff, *Phys. Rev. Lett.* **61**, 574 (1988).

<sup>6</sup>Y. K. Vohra, C. A. Vanderborgh, S. Desgreniers, and A. L. Ruoff, *Phys. Rev. B* **39**, 5464 (1989). We apologize that this reference was inadvertently omitted from our paper (Ref. 1).

<sup>7</sup>Y. K. Vohra, C. A. Vanderborgh, S. Desgreniers, and A. L.

Ruoff, *Bull. Am. Phys. Soc.* **34**, 507 (1989).

<sup>8</sup>J. A. Xu, H. K. Mao, and P. Bell, *Acta Phys. Sin.* **36**, 501 (1987).

<sup>9</sup>W. C. Moss and K. A. Goettel, *Appl. Phys. Lett.* **50**, 25 (1987).

<sup>10</sup>W. C. Moss and K. A. Goettel, *J. Appl. Phys.* **61**, 4951 (1987).

<sup>11</sup>H. K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986).

<sup>12</sup>R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **61**, 857 (1988).

<sup>13</sup>H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).

<sup>14</sup>A. L. Ruoff and Y. K. Vohra, *Appl. Phys. Lett.* **55**, 232 (1989).

<sup>15</sup>J. H. Eggert, K. A. Goettel, and I. F. Silvera, *Appl. Phys. Lett.* **53**, 2189 (1988).