

---

# TWO NEAR-COLORLESS GENERAL ELECTRIC TYPE-IIA SYNTHETIC DIAMOND CRYSTALS

By James E. Shigley, Emmanuel Fritsch, and Ilene Reinitz

---

*Gemological examination of two near-colorless, isotopically pure, carbon-12 synthetic diamonds grown recently by General Electric reveals short-wave ultraviolet luminescence behavior, a cathodoluminescence pattern, and small metallic inclusions that are typical of other gem-quality synthetic diamonds. These characteristics also help separate them from natural type-IIa diamonds. Study of additional near-colorless synthetic diamonds is needed to confirm these preliminary observations.*

---

Of all the gem-quality synthetic diamonds that could potentially enter the jewelry trade, faceted near-colorless synthetic diamonds are the greatest concern. Not only do near-colorless diamonds represent the vast majority of stones in the jewelry industry, but the techniques the jeweler typically uses to quality grade these stones are different from those needed to separate natural from synthetic diamonds. Yet relatively few near-colorless gem-quality synthetic diamonds have been made available for gemological examination, so practical means for identifying them have not been well documented.

In 1990, scientists at the GE (General Electric) Research and Development Center in Schenectady,

New York, announced the production of a new, isotopically pure carbon-12 ( $^{12}\text{C}$ ) synthetic diamond (press releases issued by General Electric Company, 10 July 1990 and 18 October 1991). Carbon in nature consists of a mixture of carbon atoms that have different masses (weights), called isotopes: 98.89% of carbon has 12 atomic mass units (usually written  $^{12}\text{C}$ ), and 1.11% of carbon has 13 atomic mass units ( $^{13}\text{C}$ ). This applies to carbon found in natural and most synthetic diamonds as well. Using isotope enrichment, one can make carbon that is almost pure  $^{12}\text{C}$  or  $^{13}\text{C}$ . Such enrichment processes are both difficult and expensive. However, the resulting isotopically pure diamond crystals have advanced technological applications related to their exceptional ability to disperse heat (Anthony et al., 1990; Banholzer and Anthony, 1992).

The very few GE  $^{12}\text{C}$  diamond crystals grown so far are only available for scientific studies; to date, none has been sold or faceted (R. D'Angelo, pers. comm., 1993). This article reports on the gemological properties and identification of two of these new GE near-colorless  $^{12}\text{C}$  synthetic diamond crystals (figure 1), and discusses how their properties compare to those of other near-colorless GE synthetic diamonds produced in the 1970s and examined by GIA at that time (Crowningshield, 1971; Koivula and Fryer, 1984). While we do not expect these near-colorless GE synthetic diamonds to appear in the jewelry industry, those from other

## ABOUT THE AUTHORS

*Dr. Shigley is director of research, and Dr. Fritsch is manager of research, at the Gemological Institute of America, Santa Monica, California. Dr. Reinitz is a research scientist at the Gemological Institute of America, New York.*

*Acknowledgments: The authors thank Rick D'Angelo of GE Superabrasives for the loan of these two crystals. The following helped in the gemological examination of these two crystals: from the GIA Gem Trade Laboratory in New York, Thomas Moses and G. Robert Crowningshield; formerly of GIA GTL New York, David Hargett; and formerly of GIA GTL Santa Monica, Christopher Smith. Mike Moon of GIA Research prepared the infrared spectra.*

*Gems & Gemology, Vol. 29, No. 3, pp. 191-197.*

© 1993 Gemological Institute of America



Figure 1. These two near-colorless synthetic diamond crystals, grown by the new GE process, were loaned to GIA by GE Superabrasives in Worthington, Ohio. Some crystal faces of these 0.91- and 1.04-ct (respectively) cuboctahedral crystals have been polished. Photo by Maha DeMaggio.

sources, grown from carbon with the standard isotopic composition or with impurities removed, could eventually become available.

### THE SYNTHESIS PROCEDURE

As with the first gem-quality GE synthetic diamonds reported in 1970, these newer crystals are grown using the standard high temperature/high pressure flux technique in what is referred to as a "belt" apparatus (figure 2; Strong and Chrenko, 1971; Bundy et al., 1973; Strong and Wentorf, 1991). A tiny (about 0.001 ct) synthetic diamond "seed crystal" (with a carbon isotope ratio of 99%  $^{12}\text{C}$  and 1%  $^{13}\text{C}$ ) is positioned in the growth vessel to initiate crystal growth. However, the synthetic diamond used as carbon-source material for this new production is quite different from the carbon (with a standard isotopic composition) that was used earlier at General Electric. The carbon-source material for this new production of large (up to about 1 ct) single crystals is actually a thin, polycrystalline layer of synthetic diamond—grown using isotopically enriched  $^{12}\text{C}$  methane gas by a low-pressure, chemical vapor deposition (CVD) technique (Anthony et al., 1990; also see Fritsch et al., 1989)—that has been crushed and powdered. In addition, the new procedure uses a transition metal flux that removes nitrogen and boron impurities, thus resulting in the crystallization of type-IIa crystals. Synthetic diamond crystals produced by this technique have ranged up to 99.9%  $^{12}\text{C}$  (with other

crystals grown by this method having up to 99%  $^{13}\text{C}$ ).

A small quantity of these new  $^{12}\text{C}$  diamond crystals have been grown, initially at the GE research facility in Schenectady, New York, and most recently at GE's commercial production facility (GE Superabrasives) in Worthington, Ohio. This research program is designed to explore the fundamentals of diamond growth and the physical-performance characteristics of this particular diamond material. Because of their isotopic purity, the thermal conductivity of the  $^{12}\text{C}$  synthetic diamonds is reportedly superior to that of natural diamonds. They are apparently also more resistant to laser damage. GE representatives are exploring the use of this new type of synthetic diamond (when cut into thin wafers—see figure 3) as heat sinks for telecommunications equipment, computers, and integrated circuits. They also envision their use as windows or mirrors in laser equipment. Manufacturing and marketing of these costly crystals for specialized, high-technology applications will be handled through GE Superabrasives in Worthington.

Figure 2. A General Electric scientist prepares the high temperature/high pressure "belt" apparatus for growing synthetic diamond crystals. Photo courtesy of General Electric.





Figure 3. One of the new GE  $^{12}\text{C}$  synthetic diamond crystals is shown here cut into slices for use in various high-technology applications. Photo courtesy of General Electric.

## MATERIALS AND METHODS

Following a visit to the GE facilities in Worthington by one of the authors (EF), representatives of GE Superabrasives loaned GIA the two  $^{12}\text{C}$  diamond crystals shown in figure 1 (as noted above, to date none of this material has been faceted). These two crystals weigh 1.04 ct and 0.91 ct.

Our examination was conducted using standard gemological testing equipment as well as more sophisticated instruments. The former included a GIA GEM Instruments binocular microscope, a long-wave (366-nm) and short-wave (254-nm) ultraviolet (U.V.) lamp unit (used in a darkened room), a Beck prism spectroscope, and a DISCAN digital-scanning, diffraction-grating spectroscope. Also used were a Pyc-Unicam 8800 ultraviolet-visible spectrophotometer and a Nicolet 60SX Fourier-Transform infrared spectrometer. Observations of cathodoluminescence were made with a Nuclide ELM-2B luminoscope. Qualitative chemical analysis was carried out by the energy-dispersive X-ray fluorescence (EDXRF) method using a Tracor X-Ray Spectrace 5000 instrument.

## RESULTS

**Crystal Morphology.** Both crystals are cuboctahedra with octahedral, cube, and other crystal faces of varying relative size and arrangement. The surface attached to the seed crystal had been polished on both crystals; on the smaller crystal, all the faces had been polished.

The octahedral faces of both crystals have the largest surface area. On the larger crystal, the trapezohedral faces are larger than the cube faces, while the reverse situation prevails on the smaller crys-

tal. The larger crystal exhibits very small dodecahedral faces.

Some surface markings, such as trigons on octahedral faces, could be seen on the larger crystal. These two crystals are similar in morphology to the yellow synthetic diamonds described previously (Shigley et al., 1986, 1987).

**Color.** For research purposes only (inasmuch as the GIA Gem Trade Laboratory does not color or clarity grade rough diamonds, either natural or synthetic), GIA GTL staff members determined that the approximate color grade of the two samples is in the "L-M" range; that is, they both exhibit a faint yellow color. No color zoning was observed. According to published reports (Anthony et al., 1990; Shor, 1990), some other new GE crystals (apparently earlier crystals, presumably grown at the GE research facility in Schenectady) have higher color grades, in the "E-G" range.

**Microscopy.** Using a gemological microscope at low to moderate magnification (10–40 $\times$ ), we saw several interesting features. The larger crystal revealed a few small, rod-like metallic inclusions (figure 4), similar to those we have seen in other synthetic diamonds. Both crystals also contained clusters or "clouds" of tiny, triangular or lozenge-shaped, tabular inclusions in areas beneath the octahedral crystal faces, as well as tiny pinpoint inclusions scattered throughout. In transmitted

Figure 4. This small, elongate, metallic inclusion was seen in the larger of the two GE  $^{12}\text{C}$  synthetic diamond crystals. Photomicrograph by John I. Koivula; magnified 40 $\times$ .



light, these tabular inclusions had low relief and a brownish appearance. In reflected light, however, they had higher relief and a bright, white or metallic, reflective appearance (figure 5). When suspended from a string, both crystals were attracted to a simple magnet, undoubtedly because of these flux metal inclusions. EDXRF analysis of the smaller crystal failed to reveal the chemical composition of these inclusions.

We did not see any graining (or fractures or cleavages) in either crystal.

While examining the two crystals between crossed polarizing filters with a gemological microscope, we saw anomalous birefringence ("strain") present as a weak, banded or clustered pattern of gray or blue (first-order and some second-order) interference colors. We also observed a weak strain pattern related to the occurrence of the large flux inclusions (see figure 6) in the larger specimen, and a weak banding of strain parallel to the cube faces of both crystals. The general absence of strain in synthetic diamonds was first reported by Crowningshield (1971) and has been routinely noted in subsequent GIA articles on the gemological properties of synthetic diamonds.

**Luminescence.** Both crystals were inert to long-wave ultraviolet radiation, but fluoresced a weak yellowish orange to short-wave U.V. The latter appeared to increase in intensity for a short period when the U.V. lamp was turned on, and then to stabilize at a certain level. One of the distinctive gemological characteristics of gem-quality synthetic diamonds is that they typically have a more

*Figure 5. Both of the GE <sup>12</sup>C synthetic diamonds revealed clusters of tiny triangular or lozenge-shaped tabular inclusions of flux metal beneath the octahedral faces of the crystal. In reflected light, these inclusions appear metallic and reflective. Photomicrograph by John I. Koivula; magnified 40x.*



*Figure 6. A weak pattern of anomalous birefringence ("strain") can be seen in the smaller crystal when it is examined between crossed polarizing filters. The black, bluish gray, and light gray are low-order interference colors indicative of weak strain. The birefringence occurs around inclusions and in a pattern related to the arrangement of internal growth sectors. Photo by John I. Koivula.*

intense response to short-wave U.V. than to long-wave U.V. (Crowningshield, 1971; Koivula and Fryer, 1984; Shigley et al., 1986, 1987; Scarratt, 1987; Rooney et al., 1993).

However, the zoning of short-wave U.V. fluorescence seen in the yellow and blue synthetic diamonds we have examined to date was not evident in either of these new GE crystals. When the short-wave lamp was turned off, both crystals continued to luminesce. This moderate greenish yellow phosphorescence persisted for more than two minutes.

We also observed the cathodoluminescence of the two crystals, that is, their luminescence when exposed to a beam of electrons in a vacuum chamber. Under these conditions, we clearly saw a zoned pattern of luminescence corresponding to the arrangement of different internal growth sectors (as has been reported in yellow synthetic diamonds; see Shigley et al., 1987).

There was, however, some difference in cathodoluminescence pattern between the two GE crystals. When viewed with its base upward, the smaller crystal exhibited large areas of slightly greenish

blue luminescence just below (and with some banding parallel to) the four octahedral faces (figure 7). Beneath the four cube faces, we observed narrow areas that formed a cross-shaped pattern with a weaker reddish luminescence (not visible in figure 7). In the larger crystal, the areas of bluish luminescence, again beneath the octahedral faces, were smaller, but the areas of weak reddish luminescence beneath the cube faces were larger. There was also a small area of bright blue luminescence in the center of this crystal. These luminescence patterns are related to the relative sizes, differences in impurity content, and different geometric arrangements of the internal growth sectors. We were surprised, however, to see stronger luminescence from the octahedral growth sectors of these crystals than from their cube sectors (in contrast to previous observations; see Shigley et al., 1987). Regardless, this zoning geometry clearly indicates the presence of different types of growth sectors, which identifies the crystals as synthetic.

When exposed to a beam of X-rays, both crystals luminesced yellow. When the X-rays were turned off, both crystals exhibited very persistent yellow phosphorescence—the larger crystal for about two minutes, and the smaller crystal for about 10 minutes.

**Electrical Conductivity.** Neither crystal proved to be electrically conductive. This directly contrasts with data reported on the near-colorless GE synthetic diamonds produced in the early 1970s (Crowningshield, 1971; Koivula and Fryer, 1984), which we determined—on the basis of their mid-infrared spectra—to be a mixed type IIa/IIb. As a result, electrical conductivity is no longer as diagnostic an identification property for near-colorless synthetic diamonds as was suggested in these articles.

**Spectroscopy.** We saw no sharp absorption bands in the visible spectra of either crystal, although we did observe a very slight increase in absorption toward the ultraviolet in both. This broad absorption at the blue end of the spectrum accounts for the faint yellow color of these crystals.

The infrared spectra of these two crystals confirmed that they are type-IIa diamonds; none of the impurity-related absorption bands that are characteristic of other diamond types were present (for information on diamond types, see Fritsch and Scarratt, 1992). This is consistent with the high-



*Figure 7. The uneven cathodoluminescence of the smaller GE  $^{12}\text{C}$  synthetic diamond results from the conditions of crystal growth, which produced an arrangement of octahedral and cube internal growth sectors that are revealed by their differing luminescence behavior. Photo by Maha DeMaggio.*

purity crystal-growth method used. Therefore, neither visible-range nor infrared spectroscopy is useful in identifying the synthetic character of these crystals.

## DISCUSSION

The gemological reports on earlier GE synthetic diamonds noted that they contained flattened or rod-like dark metallic inclusions or tiny dust-like pinpoints, exhibited no sharp bands in their visible-range absorption spectrum, and were remarkably free of "strain." Two of the faceted stones examined for these reports were color graded in the "I-J" range. In addition, these synthetic diamonds fluoresced and phosphoresced yellow to short-wave (but not to long-wave) U.V. radiation and to X-rays, and they were slightly electrically conductive. Tests such as infrared spectroscopy and EDXRF chemical analysis that are now routinely performed in gemological research were not done at that time because the instrumentation was not readily available.

The two crystals documented here have both similarities to, and differences from, early GE near-colorless synthetic diamonds—as reported by

Crowningshield (1971) and Koivula and Fryer (1984), and with information provided by three crystals (0.20 to 0.75 ct) and four faceted stones (0.29 to 0.78 ct; "F-G" and "H" color grades) subsequently examined in GIA Research. Both the older and the newer GE gem-quality synthetic diamonds have weak-to-strong yellow short-wave U.V. fluorescence (but no long-wave U.V. fluorescence), little or no "strain," metallic flux inclusions, and a visible-range absorption spectrum with no sharp bands. However, the earlier GE material is electrically conductive type-IIa/IIb diamond while, in contrast, the newer GE crystals are type-IIa diamonds, which do not conduct electricity. We are certain that these features result from differences in the growth process and are not related to the carbon isotope composition.

As part of GIA's ongoing research into synthetic diamonds, we have also begun to document type-IIa natural diamonds to help identify their distinguishing characteristics. Although to date we have studied only 30 rough and faceted type-IIa diamonds, some preliminary observations can be drawn.

These "near-colorless" natural type-IIa diamonds appeared to fall into two categories: (1) those that are slightly brownish or grayish (five of the 30), and (2) those that are essentially colorless ("D to F" color grades; 25 of the 30). Of the 30 samples, 20 were inert to both long- and short-wave U.V. radiation, and 10 exhibited a very weak or weak blue, yellow, or orange fluorescence to both wavelengths (with the long-wave reaction equal to or greater than the short-wave reaction). Although very weak U.V. fluorescence in a diamond may be difficult to see (even in a darkened room), we saw a very weak yellow or blue fluorescence to short-wave U.V.—with no fluorescence to long-wave U.V.—in only two of these natural diamonds. Only one of the 30 samples displayed any phosphorescence: a weak yellow luminescence that persisted for only a few seconds. Weak octahedral graining could be seen in almost all faceted samples, and they all exhibited a corresponding weak, cross-hatched "strain" pattern of blue and yellow or gray interference colors (with the cross-hatched pattern representing planes parallel to octahedral crystal faces). Metal inclusions are virtually unknown in natural gem diamonds (although Sobolev et al., 1981, reported the presence of metallic iron as inclusions in some natural diamonds). Nor have we ever seen triangular tabular inclusions, like

those in the two GE crystals described here, in a natural diamond. Last, the visible-range absorption spectra of the natural samples lacked strong sharp absorption bands, but two samples displayed one or more weak sharp bands (such as at 503, 515, and 575 nm). We observed no distinctive features in the infrared spectra of these 30 natural diamonds.

In general, the most useful properties to identify near-colorless GE synthetic diamonds include short-wave U.V. fluorescence and phosphorescence, metallic inclusions, yellow X-ray luminescence and phosphorescence, and zoned cathodoluminescence. The absence of anomalous birefringence is only an indication of synthetic origin, as is the observation of a visible spectrum with no sharp absorption bands. However, because we have been able to examine only a very few near-colorless gem-quality synthetic diamonds to date, we urge caution in overgeneralizing from these few observations.

When testing an unknown near-colorless diamond, a practical approach would be to check the short-wave U.V. luminescence, and to look for the presence of metallic inclusions and for the absence of both anomalous birefringence and sharp bands in the visible absorption spectrum. Since most near-colorless natural gem diamonds are type Ia, they will likely have U.V. luminescence (to both long- and short-wave radiation, with long-wave more intense than short-wave) and a visible-range absorption spectrum exhibiting one or more sharp bands ("Cape lines"). Although natural type-IIa diamonds will not show these features, they can display graining and anomalous birefringence related to their growth as octahedral crystals. In testing an unknown near-colorless diamond, it may be more useful to check for features that prove the stone is a natural diamond than to look for those that indicate that the diamond is synthetic. Use of advanced techniques such as cathodoluminescence or possibly EDXRF chemical analysis may help confirm an identification in difficult cases.

## CONCLUSION

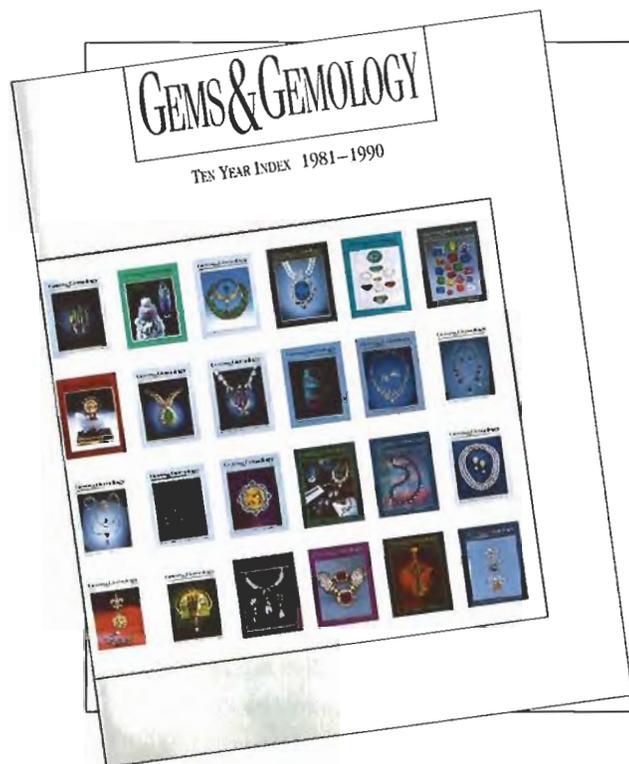
Examination of two near-colorless, isotopically pure,  $^{12}\text{C}$  type-IIa synthetic diamond crystals grown by General Electric using a new method has revealed that they have several distinctive gemological properties. Most diagnostic are luminescence to short-wave U.V. radiation (as for most synthetic diamonds reported to date), and the pres-

ence of metallic inclusions and very small triangular tabular inclusions. Further study of natural and synthetic type-IIa diamonds is needed to confirm these preliminary identification criteria. Although colored synthetic diamonds have some obvious distinctive properties, the identifying characteris-

tics of near-colorless synthetic diamonds appear to be more subtle. While there is little possibility that these GE synthetic diamonds will be sold for jewelry use, the diamond industry must anticipate the challenge of identifying near-colorless synthetic diamonds produced by other manufacturers.

## REFERENCES

- Anthony T.R., Banholzer W.F., Fleischer J.F., Wei L., Kuo P.K., Thomas R.L., Pryor R.W. (1990) Thermal diffusivity of isotopically enriched  $^{12}\text{C}$  diamond. *Physical Review B (Condensed Matter)*, Vol. 42, Third Series, No. 2, pp. 1104-1111.
- Banholzer W.F., Anthony T.R. (1992) Isotope enrichment during diamond growth. *Diamond and Related Materials*, Vol. 1, No. 12, pp. 1157-1160.
- Bundy F.P., Strong H.M., Wentorf R.H. Jr. (1973) Methods and mechanisms of synthetic diamond growth. *Chemistry and Physics of Carbon*, Vol. 10, pp. 213-263.
- Crowningshield R. (1971) General Electric's cuttable synthetic diamonds. *Gems & Gemology*, Vol. 13, No. 10, pp. 302-314.
- Fritsch E., Conner L., Koivula J.I. (1989) A preliminary gemological study of synthetic diamond thin films. *Gems & Gemology*, Vol. 25, No. 2, pp. 84-90.
- Fritsch E., Scarratt K. (1992) Natural-color, nonconductive gray-to-blue diamonds. *Gems & Gemology*, Vol. 28, No.1, pp. 35-42.
- Koivula J.I., Fryer C.W. (1984) Identifying gem-quality synthetic diamonds: An update. *Gems & Gemology*, Vol. 20, No. 3, pp. 146-158.
- Rooney M.L.-T., Welbourn C.M., Shigley J.E., Fritsch E., Reinitz I. (1993) De Beers near colorless-to-blue experimental gem-quality synthetic diamonds. *Gems & Gemology*, Vol. 29, No. 1, pp. 38-45.
- Scarratt K. (1987) Notes from the laboratory—11. *Journal of Gemmology*, Vol. 20, Nos. 7/8, pp. 406-409.
- Shigley J.E., Fritsch E., Stockton C.M., Koivula J.I., Fryer C.W., Kane R.E. (1986) The gemological properties of the Sumitomo gem-quality synthetic diamonds. *Gems & Gemology*, Vol. 22, No. 4, pp. 192-208.
- Shigley J.E., Fritsch E., Stockton C.M., Koivula J.I., Fryer C.W., Kane R.E., Hargett D.R., Welch C.W. (1987) The gemological properties of the De Beers gem-quality synthetic diamonds. *Gems & Gemology*, Vol. 23, No. 4, pp. 187-206.
- Shor R. (1990) GE's new synthetics are 'costly beauties.' *Jewelers Circular Keystone*, September, Vol. 161, No. 9, pp. 62-63.
- Sobolev N.V., Efimova E.S., Pospelova L.N. (1981) Native iron in diamonds of Yakutia and its paragenesis. *Soviet Geology and Geophysics*, Vpl. 22, No. 12, pp. 18-21.
- Strong H.M., Chrenko R.M. (1971) Further studies on diamond growth rates and physical properties of laboratory-made diamonds. *Journal of Physical Chemistry*, Vol. 75, No. 12, pp. 1838-1843.
- Strong H.M., Wentorf R.H. Jr. (1991) Growth of large, high-quality diamond crystals at General Electric. *American Journal of Physics*, Vol. 59, No. 11, pp. 1005-1008.



## Where to Find Everything You Need to Know?

### *The Gems & Gemology Ten-Year Index, 1981-1990*

Thousands of entries lead you to critical information on everything from De Beers gem-quality synthetic diamonds to Kashmir sapphires, from inclusion photography to infrared spectroscopy, from the Muzo mine to Minas Gerais to Mingxi.

An indispensable resource, the Index is your guide to the exciting developments published in *Gems & Gemology* during this decade.

You can get your personal copy for only \$9.95 (plus shipping and handling, and tax where appropriate) or FREE with your new subscription to *Gems & Gemology*.

Supplies are limited. Order NOW.

For more information, Call toll-free (800) 421-7250 x201, or outside the U.S. (310) 829-2991 x201. FAX (310) 453-4478.

Or Write *Gems & Gemology* Subscriptions Dept.,  
1660 Stewart St., Santa Monica, CA 90404