[197]Au MÖSSBAUER STUDY OF THE GOLD–SILVER DITELLURIDES SYLVANITE, KRENNERITE AND CALAVERITE: REPLY

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We welcome the comments of J. Stanek, who correctly points out that there are some uncertainties concerning the sign of the electric quadrupole inter-action in gold compounds. This is so because it is experimentally quite difficult to measure the sign of the electric quadrupole interactions of [197]Au. First of all, the measurement requires the use of oriented single-crystal absorbers. The sign of the electric quadrupole interaction can then be determined from the asymmetry of the line intensities within the quadrupole doublet, but this asymmetry remains always small for [197]Au because of the nuclear proper-ties of the 77 keV transition (Prosser *et al.* 1975). Properly oriented single-crystal absorbers alone, how-ever, are not sufficient for a determination of the sign. Rather, the crystal structure must also permit a sub-stantial alignment of the axes of the electric- field-gradient tensor in the laboratory frame of reference. This is, for instance, not necessarily the case when the unit cell contains several atoms of gold, for which these axes are oriented in different directions. The structure of the gold ditellurides and of many other gold compounds, in fact, renders a measurement of the sign of the electric-field gradients difficult or even impossible even in the case where single-crystal absorbers are available. This is why we have not attempted a determination of the sign in the case of the ditellurides.

It is mainly due to these difficulties that the sign of the electric quadrupole interaction has been deter-mined unambiguously only in $KAu(CN)_2$ (Prosser *et al.* 1975). The existence of a rather clear correlation between the quadrupole splittings and the isomer shifts for Au^+ compounds is, however, usually (see, for instance, Parish 1984) considered as proof for a negative sign for the electric quadrupole interaction in all linearly coordinated Au^+ compounds. In Au^{3+} com-pounds with a fourfold planar coordination, bonding arguments are usually used to assign a positive sign to the electric quadrupole interaction (Parish 1984). Since the sign the electric quadrupole interaction is not normally obtained from the Mössbauer spectra, one usually plots only the magnitude of the electric quadrupole interaction *versus* the isomer shifts. This results in plots like that shown in Figure 3 of our paper.

Stanek claims that the electric quadrupole interac-tion is positive in the Au^+ halides, $AuCl$ and AuI, whereas he concedes that for all other Au^+ compounds it is negative, as is commonly taken for granted. Stanek's assumption implies a tremendously large change of the electric field gradient between the monohalides and their closest neighbors on the cor-relation line, *e.g.*, the $(AuCl_2)^-$ complex anion in $(AsPh_4)AuCl_2$, for which one obtains an electric quadrupole interaction of -6.1 mm/s (sign assumed, not measured) and an isomer shift of $+0.5$ mm/s (Jones *et al.* 1977; this compound has not been included in Figure 3 of our paper). We feel that it is difficult to believe that a difference in the sign of the electric field gradient exists between the linear Cl–Au–Cl bonds in $AuCl$ and in $(AsPh_4)AuCl_2$, but since Stanek's inter-pretation hinges uniquely on the sign of the quadru-pole interaction in the monohalides of gold, the final decision between the two views can only be made by measuring the sign for at least one of these. Such a measurement is rendered difficult, though not alto-gether impossible, by the zig-zag chain structure of $AuCl$ and AuI, and also meets with the difficulty of obtaining sizeable single crystals of these com-pounds. Efforts to arrive at such a determination of the sign should, however, be made, since in this way the interesting question whether Orgel's bonding concept (Dunitz & Orgel 1960) is borne out by the

hyperfine interactions in gold compounds could be answered. Self-consistent calculations of the electric field gradients in Au^+ compounds (Guenzburger & Ellis 1980) would rather indicate a negative sign in the halides.

It is true that the electric quadrupole interactions we find for the (2 + 2 + 2) sites in the ditellurides coincide better with Stanek's correlation line than with the standard one, whichever sign one attributes to our results. We do not believe, however, that this should be considered as supporting Stanek's view. The relatively small magnitude of the quadrupole splitting in the ditellurides also can be attributed to the fact that the (2 + 2 + 2) configuration is not truly linear, but rather a distorted octahedral one in which two bond lengths are substantially shorter than the other four. Whatever kind of hybridization one invokes, such an environment should give an electric field gradient intermediate between that of an isolated linear arrangement and that of a symmetrical octahedron, which should give no electric field gradient at all.

In conclusion, we wish to reiterate that an experimental clarification of the question raised by Stanek is highly desirable and should be possible if sizeable single crystals of the gold monohalides can be grown.

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