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^{197}Au MÖSSBAUER STUDY OF THE GOLD–SILVER DITELLURIDES SYLVANITE, KRENNERITE AND CALAVERITE: DISCUSSION

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In a recent paper (Wagner et al. 1994), it has been shown that in some Ag–Au ditellurides, part of gold atoms occupies (2 + 2 + 2) sites of a quasi-linear coordination. The valence state of that fraction of gold remained unexplained: the linear coordination favors the Au$^+$ state, but the determined hyperfine parameters, i.e., quadrupole splitting (QS) and isomer shift (IS), do not, according to the authors, follow the QS–IS correlation for Au$^+$ compounds, as shown in Figure 1 (left).

The aim of this comment is to clarify the last point. The QS–IS correlation referred to has been derived with assumption of 6*s*–6*p* hybridization for all Au$^+$ compounds. The consequence of such model of bonding is the elongation of the Au atomic shell, which produces a gradient in the electric field with a negative main component, V_{zz}. In fact, the negative sign of V_{zz} has been experimentally confirmed only for the highly covalent KAu(CN)$_2$. However, for ionic compounds, a 5*d*–6*s* mixing must be considered (Orgel 1958), which, in extreme cases, may effectively compress the Au$^+$ electronic shell, leading to a positive V_{zz}. This mechanism is expected to be especially important for gold because, owing to the relativistic effects, the 5*d*–6*s* energetic separation is unusually small in this case. Accordingly, a new QS–IS correlation has been proposed (Stanek 1982), with positive values of V_{zz} for Au$^+$ halides, and with negative values for other Au$^+$ compounds, as shown in Figure 1 (right).

The sign of V_{zz} in the (2 + 2 + 2) sites of Ag–Au–Te minerals is not known. Nevertheless, owing to the small QS, the experimental data follow the new QS–IS correlation within both assignments.

In conclusion: (i) in (2 + 2 + 2) sites of the Ag–Au–Te minerals, gold is monovalent, and (ii) in these compounds, the covalent bonding (6*s*–6*p* hybridization) and ionic interactions (5*d*–6*s* mixing) nearly compensate for themselves in the sense that the total distortion of the Au electronic shell is rather small. The above considerations certainly do not contradict the results published by Wagner *et al.* (1994); on the contrary, they probably make them more interesting from the point of view of physical chemistry.

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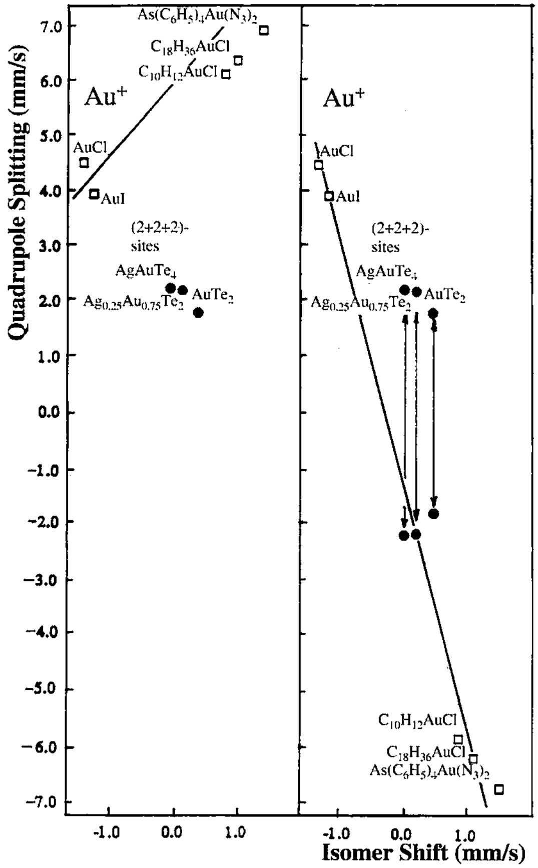

FIG. 1. Quadrupole splitting (QS) – isomer shift (IS) correlation for Au$^+$ compounds. Left: the correlation proposed by Wagner *et al.* (1994). The solid line is the assumed correlation, and full dots show the hyperfine parameters of ^{197}Au in (2 + 2 + 2) sites. Right: The solid line shows the proposed QS–IS correlation (Stanek 1982), with full dots as at left, but with two possible assignment of the sign of V_{zz}, here the sign of QS.