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Vibrational Frequencies and Pauling's Electrostatic Valence Rule

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It is to be expected that the sum of the electrostatic bond strengths received by an anion will influence the cation–anion vibrational frequency. This is illustrated on the Ti–O symmetrical stretching frequency.

Pauling's electrostatic valence rule (*1*) has received renewed interest in recent years. This rule states that p, the sum of the electrostatic bond strengths received by the anions, is on the average equal to their valancy: $p = \sum_i Z_i/n_i$, where Z is the formal charge, n the coordination number of the cations, and i the summation over the cations surrounding a specific anion. Baur (*2*) has related individual distances in a coordination polyhedron to p. Shannon et al. (*3*) applied these relations to derive bond-strength–bond-length curves and rules predicting the cation coordination in normal and high-pressure oxides. We showed that the cation coordination in apatites can be predicted simply in this way (*4*). All these applications of Pauling's rule are in the field of pure crystal chemistry. It may be expected, however, that physical properties determined by electrons localized in certain cation–anion bonds can also be predicted with some accuracy by Pauling's rule. Examples are scarce, however. The only case we are aware of is the relation between p and the position of the first charge-transfer transition of octahedral complexes consisting of a central metal ion with p^6d^0 configuration (e.g., Ti^{4+}, Nb^{5+}, W^{6+}) and six oxygen anions (*5*). At the same time p determines the position of the emission band and the thermal quenching temperature of the luminescence of these complexes.

Baur's relation between p and the cation–anion distance suggests that it should be possible to relate the value of p to the cation–anion vibrational frequency. As a matter of fact such an influence can only be observed for vibrational modes that are strongly localized in the crystal. In this note we report a relation between p and the Ti–O stretching frequency in oxides.

A low value of p, i.e., a too-low number of cations around an anion, will result in a strong cation–anion bond and, therefore, a high stretching frequency. In Fig. 1 we have plotted the frequency of localized, symmetrical Ti–O stretching frequencies versus the value of p for the relevant oxygen ion. The result is a strong evidence for a relation between p and the value of the stretching frequency and explains at the same time the large spread in Ti–O stretching frequencies found in the literature. Such a relation may be of some use in the assignment of vibrational spectra. Its application will, however, be restricted due to the fact that vibrational modes in solids are often not localized.

Finally we will account for the crosses in Fig. 1. The data for $NaLnTiO_4$ have been explained in (*6*). They relate to the strong Raman lines around ~900 and ~600 cm^{-1} which are ascribed to the Ti–O stretching vibrations along the z-axis. The same holds for $Bi_4Ti_3O_{12}$. The low frequency value of 550 cm^{-1} has not been reported before and is the maximum of a broad band with some structure in the Raman spectrum. The value for La_2MgTiO_6 follows directly from (*7*). The

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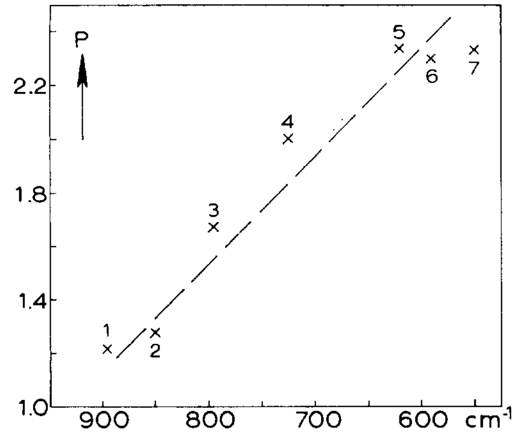

FIG. 1. The value of p vs the frequency of the relevant symmetrical Ti–O stretching frequency. Points 1 and 5 relate to $NaLnTiO_4$ (average values), 2 and 7 to $Bi_4Ti_3O_{12}$, 3 and 6 to Ln_2TiO_5 (average values), and 4 to La_2MgTiO_6. See text also.

high-frequency value for Ln_2TiO_5 has been given by Paques-Ledent (*8*); the relevant crystal structure by Müller-Buschbaum *et al.* (*9*). For the other symmetrical Ti–O stretching vibration (*8*) gives 555 cm^{-1} for Nd_2TiO_5. The relevant value of p is 2.3. In the series Ln_2TiO_5 this frequency varies strongly up to values of about 620 cm^{-1} (*8*). These values obey the given relation. The present values are derived from the spectra of titanates with titanium in six- or five-coordination. It is well-known from the work of Tarte (*10*) that the value of the stretching frequencies depends on the coordination (e.g., tetrahedral or octahedral) of the metal ion. This fact restricts the use of relations such as those in Fig. 1 even further.

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