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I. N. Pen' kov, I. A. Safin

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Abstract

Full Text

Physical Chemistry

I. N. Pen' kov, I. A. Safin

Nuclear Quadrupole Resonance in Orpiment

(Presented by Academician B. A. Arbuzov, 30 XII 1963)

In work ([1]) the observation was reported of the spectrum of nuclear quadrupole resonance (n.q.r.) of As^{75} nuclei in orpiment—natural arsenic sulfide (As_2S_3). In the present work additional experimental results of the study of n.q.r. in this compound and their interpretation are given.

The crystal lattice of orpiment is built of coordination complexes AsS_3, having the form of a trigonal pyramid with the As atom at the vertex (Fig. 1). The complexes are assembled into infinite chains and nets perpendicular to the monoclinic b axis. The As–S distances in the complexes are 2.15, 2.20, and 2.35 Å. The valence angles have the values: ∠S–As–S = 94, 97, and 100°; ∠As–S–As = 88 and 106°. The shortest distances between the nets along the As–S line considerably exceed the corresponding distances in the complexes, which accounts for the very perfect cleavage in the single crystal along (010). The As_2S_3 cell belongs to the space group $P2_1/n$. Its parameters are as follows: $a_0 = 11.49$, $b_0 = 9.59$, and $c_0 = 4.25$ Å; $\beta = 90°27'$ ([2]).

The n.q.r. spectrum of As^{75} nuclei (spin I equal to 3/2) was studied at temperatures of 77 and 300°K. The following were investigated: cleavage fragments (plates perpendicular to the b axis), polycrystalline masses, and artificially prepared powders of orpiment samples from the Lukhumskoe (Caucasus) and Min' kole (Yakutia) deposits.

For all orpiment samples the n.q.r. spectrum consists of two lines of equal intensity, the resonance frequencies of which are given in Table 1.

Table 1

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Sample	Position of the As^{75} nucleus in the unit cell As_2S_3	Resonance frequency, ν_{res}, MHz, $\pm$ 0.005, 300°K	Resonance frequency, ν_{res}, MHz, $\pm$ 0.005, 77°K	Resonance-line width $\Delta\nu$, kHz, 300°K	Spin-lattice relaxation time T_1, sec., 300°K	Quadrupole coupling constant eQq, MHz, 300°K (at $\eta = 0$)
Cleavage fragment (Min' kole)	I	69.547	70.336	140	0.027	130.09
Cleavage fragment (Min' kole)	II	71.942	72.804	100	0.033	143.88
Powder (particle size 200 mesh, Lukhumskoe deposit)	I	69.544	70.331	200		
Powder (particle size 200 mesh, Lukhumskoe deposit)	II	71.942	72.796	140		
Polycrystal (Lukhumskoe deposit)	I	69.547	70.324	115		

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Sample	Position of the As^{75} nucleus in the unit cell As_2S_3	Resonance frequency, ν_{res}, MHz, ± 0.005, 300°K	Resonance frequency, ν_{res}, MHz, ± 0.005, 77°K	Resonance-line width $\Delta\nu$, kHz, 300°K	Spin-lattice relaxation time T_1, sec., 300°K	Quadrupole coupling constant eQq, MHz, 300°K (at $\eta = 0$)
Polycrystal (Lukhumskoe deposit)	II	71.932	72.793	80		

From a spectrum of this kind it follows that in the unit cell of orpiment one should distinguish two sorts of coordination complexes AsS_3, which do not coincide with one another under any symmetry transformations. Since the resonance frequencies differ relatively little, it may be assumed that the crystal-chemical nonequivalence is caused by small distortions in the symmetry of the complexes, due in turn to the action of interplanar forces. This agrees with the structural data: one of the As–S distances between nets within the cell is shorter than the sum of the van der Waals radii of As and S (3.85 Å). Of small one-

lateral compression of the cell in the direction of the b axis is quite sufficient to cause detectable N.Q.R. changes in the electronic environment of the resonant nuclei. We attribute the shortening of the distance between the networks to the combined action of donor–acceptor and van der Waals bonds ([3]). Starting from such a model, one can explain the observed differences in the values of the quadrupole coupling constants eQq in orpiment and assign the nonequivalent As atoms in its unit cell. The corresponding values of eQq are given in Table 1.

An analysis of the electronic configurations of the As and S atoms and of the symmetry of the coordination complexes AsS_3 shows that the principal contribution to the electric-field gradient q at the As^{75} nuclei for both positions is due to the ionic component of the As–S bond in the complexes and to sp^3 hybridization of the bonding orbitals. The difference in the magnitudes of the effective charges of the As atoms, owing to the manifestation of donor–acceptor bonds, makes it probable that weak bonds of the As–As type are present in the chains –As–S–As–(Fig. 1). The latter explains, to some extent, the related character of the structures of orpiment and realgar ([4]); in realgar such bonds are established by ordinary methods.

Fig. 1. Unit cell of As_2S_3 in projection onto the plane ab. Interatomic distances are given in angstroms.

In the measurements, the pulse method of nuclear quadrupole echo was used ([5]).

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Fig. 1. Unit cell of As2S3 in projection onto the ab plane. Interatomic distances are given in angstroms.

Figure 1: Fig. 1. Unit cell of As2S3 in projection onto the ab plane. Interatomic distances are given in angstroms.

The durations of the probing pulses were of the order of 2-3 μsec. The large width of the resonance lines makes the study of orpiment single crystals in a magnetic field difficult, and therefore the values of the asymmetry parameter η for different positions were not determined. However, the experimental facts indicate that the value of η for type I nuclei must be larger than for type II nuclei. Therefore the difference in the values of the quadrupole coupling constants eQq (which are determined from the expressions for the N.Q.R. resonance frequencies,

$$\nu_{\text{res}} = \frac{eQq}{2}\left(1+\eta^2/3\right)^{1/2}$$

with allowance for finite values of η) will be greater than for the case $\eta = 0$.

The changes of the resonance frequencies with temperature for the two nonequivalent positions of the As^{75} nuclei correlate with the values of the spin-lattice relaxation times T_1 (Table 1). The Bayer mechanism ([6]) (the amplitudes of torsional or other motions of atoms in the vicinity of type I nuclei should exceed those in positions II), as well as diffusion of defects in the orpiment lattice, may be responsible for spin-lattice relaxation.

In accordance with the symmetry and position of the AsS_3 complexes in the orpiment lattice (Fig. 1), the orientation of the axes of the electric-field-gradient tensors z_1 and z_2 may, in a first approximation, be taken to be along the crystal b axis. The axes z_1 and z_2 are not equivalent electrically; this gives rise to an additional anisotropy in the properties of orpiment single crystals, manifested, for example, in a number of optical effects ([7]).

In N.Q.R., the degree of perfection of the crystal structure determines the width of the resonance line when the latter exceeds 1-5 kHz. A constant source of broadenings is various kinds of defects of the crystal lattice, especially dislocations ([8]). The difference in the observed widths of the resonance lines can be explained by the lower symmetry

electronic wave function for positions I of the As^{75} nuclei in the orpiment cell. The asymmetry parameter η for positions I must be considerably larger in magnitude than for type-II nuclei. Owing to the different magnetic surroundings, the character of the dipole and exchange interactions of the As nuclei in the two nonequivalent positions will not be the same. The nearest magnetic neighbor of As_{II} is an As_I nucleus at a distance of 3.28 Å (Fig. 1), whereas As_I has two neighbors—As_{II} (3.28 Å) and As_I from the neighboring network (3.86 Å). This, as well as the influence of the Earth' s magnetic field, apparently explains the

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Fig. 2. Envelopes of the quadrupole-echo signals of As75 nuclei in As2S3 as a function of the interval between two pulses at 300°K for two nonequivalent positions I and II

Figure 2: Fig. 2. Envelopes of the quadrupole-echo signals of As75 nuclei in As2S3 as a function of the interval between two pulses at 300°K for two nonequivalent positions I and II

different decay of the amplitudes of the quadrupole-echo signals as a function of the interval between the probing pulses (Fig. 2). Since the content of the magnetic isotope S^{33} is 0.74%, its influence may be neglected.

Fig. 2. Envelopes of the quadrupole-echo signals of As^{75} nuclei in As_2S_3 as a function of the interval between two pulses at 300° K for two nonequivalent positions I and II

The experimental values of the widths of the resonance lines suggest localization of the maximum dislocation density in the vicinity of type-I As^{75} nuclei. As is seen from the data of Table 1, changing the temperature of the samples from room temperature to liquid-nitrogen temperature has little effect on the line width $\Delta\nu$. The values of $\Delta\nu$, as well as the form of the envelope of the quadrupole-echo signals (Fig. 2), do not change appreciably after annealing, prolonged irradiation of the sample by a Ra–Be neutron source ($\sim 10^5$ neutrons/sec $\cdot$ cm^2), and pressure up to 10^4 atmospheres. Thus, the natural distribution of dislocation density is an equilibrium one, arising in the process of growth of orpiment crystals under natural conditions.

It is also of interest that in orpiment, after melting and repeated annealing, we did not find traces of the NQR spectrum, although in natural samples quadrupole-echo signals are observed on the oscilloscope screen with a signal-to-noise ratio of the order of 100. A control X-ray structural analysis in this case also showed the absence of a diffraction pattern.

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