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1962

SovietRxiv

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Abstract

Full Text

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Nuclear Quadrupole Resonance in Stibnite

(Presented by Academician B. A. Arbuzov, June 29, 1962)

Stibnite—a mineral of composition Sb_2S_3—crystallizes in the rhombic system, space group $D_{2h}^{16}-Pbnm$, with lattice constants: $a = 11.20$ Å, $b = 11.28$ Å, $c = 3.83$ Å. The lattice is built of zigzag Sb—S—Sb chains forming ribbons. The latter are oriented parallel to the *a* and *c* axes, which accounts for the perfect cleavage along (010) ([1]). In the unit cell of stibnite there are two chemically nonequivalent positions for Sb atoms, which in Fig. 1a are denoted as A and B. The coordination complexes A are brought into coincidence with one another by rotations or mirror reflections and subsequent parallel translations. An analogous situation occurs for the coordination complexes B. However, complexes A and B are not brought into coincidence with each other by any symmetry transformations.

Nuclear quadrupole resonance (N.Q.R.) for the A positions of Sb nuclei in Sb_2S_3 was observed by Wang ([2]); data for position B are absent from the literature. In the present work we give the results of investigations of the N.Q.R. spectrum of Sb^{121} and Sb^{123} nuclei in Sb_2S_3 for both positions A and positions B. Since the spins of the Sb^{121} and Sb^{123} nuclei are respectively 5/2 and 7/2, there are in all 10 transitions, the frequencies of which are given in Table 1 for temperatures of 300° K and 77° K. For each of the positions A and B, the directions of the principal axes of the electric-field-gradient tensor relative to the crystal axes were found, and certain relaxation parameters were determined.

Fig. 1. Unit cell of stibnite in projection onto the *ab* plane of the crystal (top) and relative orientations of the crystal axes and the principal axes of the electric-field gradient for the A and B positions of $Sb^{121},^{123}$ nuclei. Interatomic distances are indicated in Å.

Method

In detecting and studying N.Q.R. in Sb_2S_3 we used a pulse technique for observing the nuclear quadrupole echo (3). The substance under investigation is acted upon, with an interval τ, by two short intense pulses of a radio-frequency magnetic field with durations t_m and $2t_m$, after which transient processes in the sample are observed. A feature of this method is the circumstance that the initial amplitude of the N.Q.R. signal from a given sample does not depend on the width of the observed line (provided t_w is such that the spectrum of the radio-frequency pulse completely covers the width of the N.Q.R. line, i.e., all resonant nuclei in the sample are excited). The pulse technique makes it possible to search for and detect N.Q.R. signals inaccessible to ordinary stationary methods. The accuracy of measuring the frequency of an N.Q.R. absorption line with this method of investigation is 10^{-4}–10^{-5}. In determining the asymmetry parameter of the electric-field-gradient tensor for the B positions of the Sb nuclei, we used the results of numerical solutions of the corresponding secular equations tabulated by Cohen (4).

Table 1

Position of nuclei in unit cell	Transition	Resonance frequency, MHz (300°K)	Resonance frequency, MHz (77°K)	T_2', μsec $\pm$10% (300°K)	T_2', μsec $\pm$10% (77°K)	$\Delta\nu$, kHz $\pm$10% (300°K)	$\Delta\nu$, kHz $\pm$10% (77°K)	eQq/h, MHz, 77°K	$d\nu/dT$, kHz/degree
A	Sb^{121} ±1/2 ↔ ±3/2	44.35	47.71	104		23	26	318.0	15.1
A	±3/2 ↔ ±5/2	88.69	95.41	79	980	34	40	318.0	30.1
A	Sb^{123} ±1/2 ↔ ±3/2	26.93	28.96				18	405.4	9.1
A	±3/2 ↔ ±5/2	53.85	57.90		1550	24	27	405.4	18.2
A	±5/2 ↔ ±7/2	80.86	86.86		1680		34	405.4	27.3
B	Sb^{121} ±1/2 ↔ ±3/2	40.99	42.98			26	26	238.3	8.9
B	±3/2 ↔ ±5/2	69.59	73.29			46	54	238.3	16.6

Position of nuclei in unit cell	Transition	Resonance frequency, MHz (300°K)	Resonance frequency, MHz (77°K)	T_2', μsec $±$10% (300°K)	T_2', μsec $±$10% (77°K)	$\Delta\nu$, kHz $±$10% (300°K)	$\Delta\nu$, kHz $±$10% (77°K)	eQq/h, MHz, 77°K	$d\nu/dT$, kHz/degree
B	Sb^{123} ±1/2 ↔ ±3/2	30.84	32.27				37	303.8	6.4
B	±3/2 ↔ ±5/2	40.99	43.13				33	303.8	9.6
B	±5/2 ↔ ±7/2	64.13	67.45				37	303.8	14.9

Zeeman splittings. The directions of the principal axes of the electric-field-gradient tensor were determined from observations of the Zeeman splittings at various orientations of the external constant magnetic field relative to the axes of the single crystal* at a temperature of 77°K. The external magnetic field, equal to 243 Oe, was produced by Helmholtz coils. For positions A of the Sb nuclei the asymmetry parameter of the electric-field-gradient tensor is equal to 0.8%; therefore it may be assumed that, in the external field H_0, the resonance line for the transition ±3/2 ↔ ±5/2 of Sb^{123} is split into two components with frequencies $\nu = \nu_0 + \gamma H_0 \cos\theta$ (ν_0 is the NQR line frequency at $H_0 = 0$). Here θ is the angle between the direction of the external magnetic field and the quantization axis Z (the symmetry axis for the electric-field gradient), and γ is the gyromagnetic ratio for Sb^{123} nuclei, equal to 552 Hz/Oe. The results of the measurements for positions A of the Sb nuclei are as follows. 1) For any orientation of the magnetic field relative to the crystal axes, no more than 4 lines were observed, i.e., for positions A there are only two systems of principal axes of the electric-field-gradient tensor. 2) If the magnetic field is oriented in the ac plane of the crystal, then the NQR line is not split when H_0 is directed along the c axis, and it breaks up into two components for other directions of the field in the specified plane. Consequently, the z-axes of the two systems of principal axes of the electric-field-gradient tensors lie in the ab plane (make an angle of 90° with the c axis) and are equally inclined to the ac plane, since the NQR line splits into only two components. The splitting of the NQR line is maximal for the field direction along the a axis and amounts to $\gamma H_0 \cos\theta = 57.9$ kHz, whence the angle of inclination of the axes of the two systems to the crystal a axis is $56 \pm 1°$. Observations at other orientations of the magnetic field confirm these conclusions.

For positions B of the Sb nuclei the asymmetry parameter is 38.1%, and the pattern of Zeeman splittings for the transitions ±1/2 ↔ ±3/2 and ±3/2 ↔ ±5/2

Fig. 2

Figure 2: Fig. 2

becomes considerably more complicated. However, for the transition ±5/2 ↔ ±7/2 the splitting pattern differs little from the case in which the asymmetry parameter is zero (4). Therefore, for this transition it may be considered that each NQR line splits into two components whose frequencies are $\nu = \nu_0 + \gamma H_0 \cos\theta$. When the magnetic field is oriented in the *ac* plane, then for any direction of the field H_0 only one unsplit line is observed, i.e., the *z*-axes of the systems of principal axes of the electric-field-gradient tensors for positions B of the Sb nuclei coincide with the *b* axis of the crystal. The splitting patterns at other orientations of the magnetic field agree with this conclusion.

It is usually assumed that NQR absorption lines have a Gaussian shape. Under this assumption, the form of the nuclear quadrupole echo signal is also described by the Gaussian function

$$\exp\left[-\frac{1}{2}\left(\frac{t-2\tau}{T_2^*}\right)^2\right],$$

which is also observed—

* Single crystals from the Sikoku deposit (Japan) were used for the measurements.

is obtained experimentally for the case of NQR of Sb nuclei in Sb_2S_3. The width parameter T_2^* for a resonance line having a Gaussian shape can be written as

$$T_2^* = \frac{\Delta t}{2.36} = \frac{0.37}{\Delta\nu},$$

where Δt and $\Delta\nu$ are, respectively, the widths of the nuclear quadrupole echo signal and of the NQR line between points whose height is one-half of the maximum.

Fig. 2. Photographs of the envelopes of nuclear quadrupole echo signals. *a*—for A positions of ^{121}Sb nuclei in the Sb_2S_3 unit cell at 300° K; *b*—for A positions of ^{121}Sb nuclei at 77° K; *c*—for B positions of ^{121}Sb nuclei at 77° K. On the left—the transition ±1/2 ↔ ±3/2; on the right—the transition ±3/2 ↔ ±5/2. The oscilloscope sweep scales are, for *a*, 40 μsec/cm, and for *b* and *c*, 200 μsec/cm. The oscilloscope sweep is triggered by the second (180°) pulse.

The experimentally observed T_2^* for Sb nuclei in Sb_2S_3 are apparently due to the combined action of dislocations and other defects in the crystal. T_2^* depends little on temperature, whereas T_2' (the nonsecular part of the NQR line width, which determines the shape of the envelope of the quadrupole-echo signals) changes with temperature (Fig. 2). A probable explanation of this effect may be the assumption that at room temperature the shortening of T_2' is caused by diffusion of defects [5] in the Sb_2S_3 lattice, and that at a temperature of 77° K the efficiency of this relaxation mechanism decreases. A study of the dependence of T_2' and T_1 (the spin-lattice relaxation time) on temperature could clarify the nature of the relaxation mechanism responsible for the changes in T_2'.

For a rigid lattice it is usually assumed that the envelope of quadrupole-echo signals obeys the law $\exp\left[-(t/T_2')^2\right]$; therefore Table 1 gives the values of T_2' found from functions of this form. The shape of the envelope of echo signals for the transitions $\pm 1/2 \leftrightarrow \pm 3/2$ differs sharply from the case of the other transitions. An explanation of this experimental fact may be

It may be supposed that, because of the multiplet structure of the NQR lines, "beats" of the bending echo are observed (6,7). The splitting of the NQR line into several components can apparently be explained by an indirect J_1J_2-exchange interaction of the nuclear spins of $Sb^{121,123}$. The Earth' s magnetic field makes a certain contribution to the indicated pattern of "beats." The temperature gradient of the NQR frequency, $d\nu/dT$, as is seen from the data of Table 1, is appreciably larger for position A of the Sb nuclei than the corresponding quantities for position B. In addition, the spin-lattice relaxation times of type-A nuclei are shorter than for type-B nuclei (for example, in the case of the transitions $+1/2 \leftrightarrow +3/2$, T_1 for positions A and B at 77°K is, respectively, $4.3 \cdot 10^{-3}$ and $11.8 \cdot 10^{-3}$ sec., ±10%).

The character of the chemical bonds in coordination complexes A and B. In the ground state, Sb and S atoms have the configurations of the outer electron shells $5s^25p^3$ and $3s^23p^4$, respectively. The experimentally observed eQq–constants of the quadrupole coupling (q.c.c.)–indicate that the Sb–S bond in the structure of stibnite has an appreciable ionic character. In the case of Sb_2S_3, the participation of only p-electrons in the bonds would lead to a spherically symmetric electronic environment of the Sb nuclei and, accordingly, to small values of the q.c.c. Hence it should be assumed that the observed q.c.c. are due to the formation of hybrid bonds. The hybridization of the bonds is indicated to some extent by the values of the valence angles in coordination complexes A and B, which differ noticeably from 90°. For complexes A one should assume sp-hybridization of the bonds, which is also confirmed by the symmetric pyramidal form of the complex and by the value of the valence angle, equal to $\sim 99^\circ$. An estimate of the s-character of the bond from the known formula

$$\alpha = \frac{\cos\theta}{\cos\theta - 1}$$

(θ is the valence angle) gives, for complex A, a value of about 13%. The smaller values of the q.c.c. for complexes B are apparently due to participation in the bonds of the d-orbitals of the Sb atoms. In this case the antimony atom in the complex under consideration is an acceptor with its free five *d*-orbitals, while the sulfur atom is a donor of its unshared $3s$ and $3p$ electron pairs. As a result, two additional bonds appear, causing the formation of the dimeric group Sb_4S_6 (Fig. 1a), which is the basic structural unit of the stibnite lattice. This is associated with an increase in the multiplicity of one of the Sb–S bonds, whose length (2.37 Å) is smaller than the sum of the covalent radii of Sb and S (2.45 Å). It is known that an increase in bond multiplicity hinders the rotational motion of complexes. The latter probably explains the difference in the magnitudes of the spin–lattice relaxation and of the temperature gradient of the NQR frequency for Sb nuclei in complexes A and B. From what has been said above it follows that complexes B are the result of the process of dimerization of Sb_2S_3 molecules.

In artificial Sb_2S_3 samples it is not possible to observe the NQR effect, although X-ray studies show them to be identical with the natural material. The NQR spectrum becomes detectable only in annealed artificial samples; in this case the NQR resonance lines have widths of about 200 kc. It may be supposed that the absence of an NQR signal in artificial samples is connected with a considerable broadening of the NQR spectrum lines (more than 500 kc) because of incomplete ordering of the lattice.

The authors are grateful to B. M. Kozyrev, A. I. Rivkind, and V. M. Vinokurov for discussion of the results.

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of the Academy of Sciences of the USSR

Received
22 VI 1962

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Note: Figure translations are in progress. See original paper for figures.