Positive Temperature Dependence of Quadrupole Splittings in Mössbauer Spectra of $Fe_{1.33}Nb_{2.67}Se_{10}$

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The Mössbauer effect in the low-dimensional compound $Fe_{1.33}Nb_{2.67}Se_{10}$ has been examined between 78 and 414 K. An anusual positive temperature dependence of the quadrupole splittings was found above 250 K. As a possible origin a mechanism due to π bonding is suggested.

Key words: Low-Dimensional Compound; $Fe_{1.33}Nb_{2.67}Se_{10}$; Mössbauer Effect; Quadrupole Splittings; π Bonding.

1. Introduction

A low-dimensional compound $Fe_{1.33}Nb_{2.67}Se_{10}$ has attracted much interest because of its charge density wave (CDW) transition below 140 K [1], similar to that in $NbSe_3$. The crystal structure is determined with X-ray diffraction to be monoclinic [2]. The structure consists of two $NbSe_6$ trigonal prismatic chains and a double chain of edge-shared $(Fe/Nb)Se_6$ octahedra, both running along the b axis. The nearly octahedral sites surrounded by six Se atoms are randomly occupied by Fe and Nb atoms with a ratio of 2:1, so that there are three kinds of unequivalent Fe atoms, Fe(2), Fe(1), and Fe(0), the number of nearest neighboring Fe atoms being indicated in the parentheses. Their ratios are 4:4:1. The CDW associated with a spot $q_1 = (0, 0.27, 0)$ in the X-ray scattering was considered to occur primarily on the prismatic chain. Besides, diffuse spots $q_2 = (0.5, 0.33, l)$ were observed to grow with decreasing temperature [3]. The latter spots were attributed to partial ordering of the metal atoms on the octahedral chain.

A localized moment observed in the study of the magnetic susceptibility indicates the existence of unpaired electrons [4]. The electric resistivity rapidly rises below the CDW transition temperature [1]. The Mössbauer experiment of this compound has been so far limited within below 300 K [4, 5]. We have extended the temperature range of the experiment up to 414 K and found that the quadrupole splittings (QS's) increase with temperature above 250 K. In this paper we present the data of the temperature dependence of the spectrum and discuss the origin of the positive temperature dependence.

2. Experiment

The compound was synthesized from its elements. They were powdered, and mixed with the appropriate composition and then reacted in an evacuated quartz tube at 700 °C. The needle-shaped crystals were selected from the product to avoid contamination due to other phases, and they were powdered again to avoid a preferred orientation causing asymmetry of the Mössbauer spectrum. The velocity of the source was calibrated with the spectrum of an α-Fe absorber, and the isomer shift was measured relative to the absorption peak of the stainless steel. First, the spectra were taken at typical temperatures with sufficiently long times, and then several spectra were taken below 196 K and above 311 K, respectively, to examine the temperature dependence, though with somewhat large statistical errors.

3. Results and Discussion

The spectra at typical temperatures are shown in Fig. 1 (a). The detailed temperature dependence is

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Table 1. Quadrupole splittings, isomer shifts δ, and relative intensities I for two doublets A and B at typical temperatures.

T (K)	QS (mm/s)		δ* (mm/s)		I	
	A	B	A	B	A	B
78	0.76	0.39	0.59	0.60	0.58	0.42
198	0.72	0.31	0.54	0.54	0.55	0.45
292	0.99	0.33	0.50	0.48	0.47	0.53
353	1.10	0.41	0.48	0.46	0.47	0.53

* The isomer shift is relative to the stainless steel.

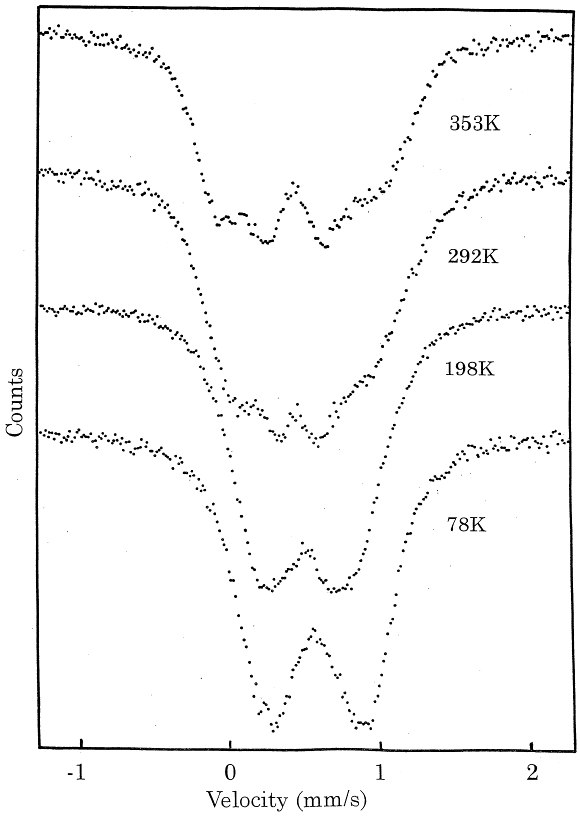

Fig. 1 (a) Mössbauer spectra of $Fe_{1.33}Nb_{2.67}Se_{10}$ at typical temperatures.

shown in Fig. 1 (b) for below 196 K and in 1 (c) for above 311 K. Four absorption peaks are clearly seen over a wide temperature range. However, if all Fe sites possess nonvanishing electric field gradients (EFG's), three doublets should be observed. One weak doublet for Fe(0) is therefore considered not to be resolved in our spectra. Thus, the spectra were analyzed as a superposition of two symmetric doublets possessing different quadrupole splittings (QS's) and intensities.

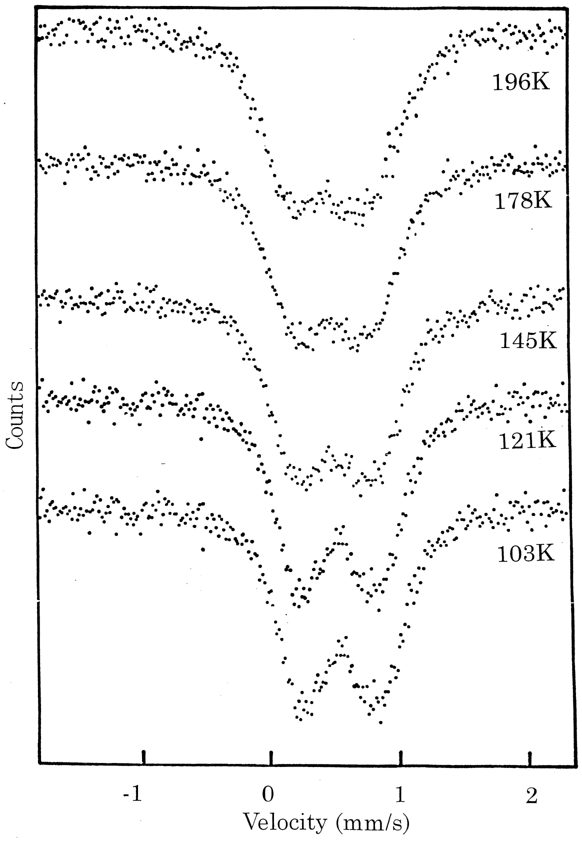

Fig. 1 (b) Mössbauer spectra of $Fe_{1.33}Nb_{2.67}Se_{10}$ at low temperatures.

The outer and inner doublets are labelled A and B, respectively. The analysis was done using a program MossWinn. The resulting temperature dependence of QS's is shown in Figure 2. Above 250 K both QS's increase remarkably. The values of QS's for the spectra in Fig. 1 (a) are listed in Table 1 together with the values of the isomer shifts and the relative intensities. Since the second-order Doppler shift is estimated to be 0.073 mm/s at 300 K, the pure isomer shift has a more negative temperature dependence.

The spectra up to 300 K were also reported by Brill et al. [5]. They analyzed the spectra as a single doublet below 160 K, regarding the doublet B as disappearing. In contrast to their analysis, our spectra could be resolved into two doublets even at 78 K, where the intensity ratio of B to A was 0.72. When the metal atoms in the double octahedral chain are completely ordered as -Fe-Fe-Nb-, only one doublet corresponding to Fe(1) site is expected. Our result therefore indicates that the ordering still continues to

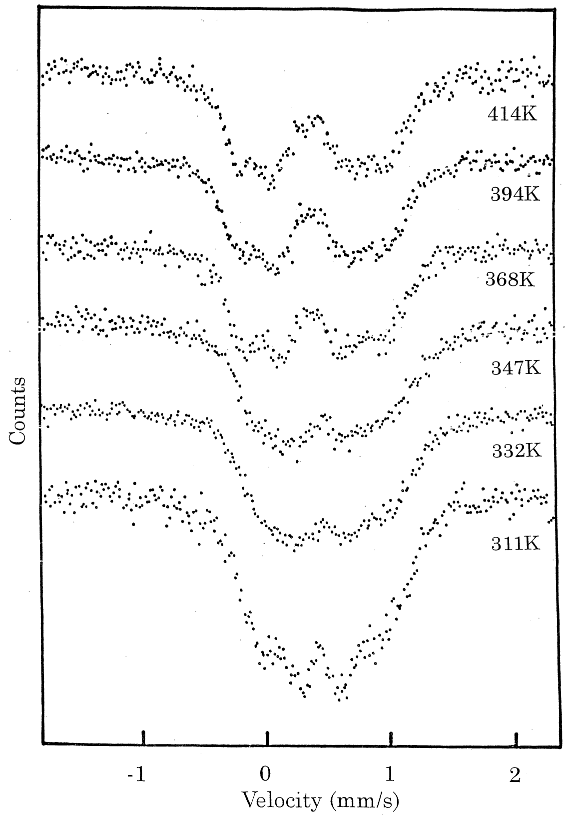

Fig. 1 (c) Mössbauer spectra of $Fe_{1.33}Nb_{2.67}Se_{10}$ at hight temperatures.

grow even at 78 K. However, the QS for the doublet B approaches that for A at low temperatures.

For nuclear spin $I = 3/2$, the QS is given by $(1/2)e^2Qq(1 + \eta^2/3)^{1/2}$ with the nuclear quadrupole moment Q, the magnitude q of the largest component of the EFG and the asymmetry parameter η. Since q usually decreases with increasing temperature owing to the thermal averaging either of the electron configuration or the orientation of the EFG tensor, some mechanism is required to explain the unusual positive temperature dependence observed in our spectra.

Above the CDW transition temperature any structural phase transition to which the positive dependence could be attributed has not been reported. The electronic state of the Fe atoms has been discussed in a number of compounds. In the crystalline field of octahedral symmetry the 3d states of the Fe atoms are split into the upper d_γ and the lower d_ϵ states, and they are further split in the environment with deviation from the octahedral symmetry. If, with increase of temperature, the d electron is raised from the Fe^{3+} low spin state to the Fe^{2+} high spin state, q may increase because the latter state usually exhibits a large q. However, the isomer shift is then also expected to increase or at least to show an upward deviation from the linear decrease, unlike the linear decrease seen in Table 1. On the other hand, the result of the band calculation [6] was reconciled with the existence of unpaired electrons by supposing an Fe^{3+} low spin state ($S = 1/2$). The formal charge of the Fe atom, +3, is also derived by assigning −2 for Se atoms and +6 for all Nb atoms in accordance to the assignment in $NbSe_3$. Then, there is a hole in the highest d_ϵ orbital, causing a nonvanishing EFG. The importance of covalency for the EFG has been shown in a number of substances [7]. In the present case, the octahedral symmetry is favorable to formation of π bond between the central metal atom and Se atoms at the corners. The formation of π bond decreases q because of accomodation of the p electron from the Se atom. The weakening of the π bonding due to thermal vibrations consequently recovers q through the back-donation of the p electron. In other words, π bonding effectively mixes the Fe^{2+} low spin state into the Fe^{3+} low spin state, and thermal vibrations purify the latter state.

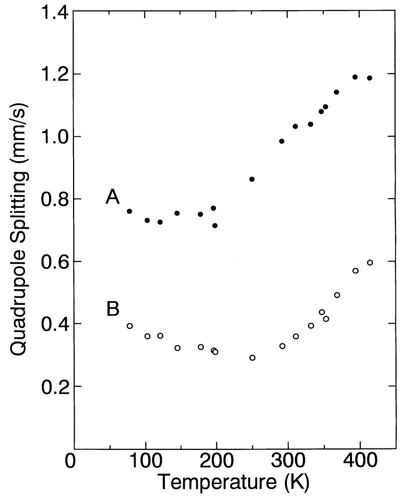

Fig. 2. Temperature dependence of Quadrupole Splitting. Both QS's increase remarkably above 250 K.

The mechanism of positive temperature dependence of the EFG due to π bonding was first proposed for the ligand chlorine NQR in the series of compounds K_2MCl_6 (M = Pt, Ir, Os, Re, and W) [8]. It was also applied to the metal NQR in the transition metal pentahalides composed of two edge-shared octahedra [9]. According to Haas and Marram, the change of q at the ligand nucleus due to π bonding from the absolute zero to temperature T is represented as

$$\Delta q = 5V \frac{H_{12}}{E_2 - E_1} C_1^0 C_2^0 \left[\frac{\hbar}{I\omega} \frac{1}{\exp(\hbar\omega/kT) - 1} \right] q_{\mathrm{at}}, \tag{1}$$

where V is the product of the number of bending modes and the number of vacancies in the π anti-bonding orbital. H_{12} is the magnitude of interaction between p_π and d_π orbitals. C_1^0 and C_2^0 are the coefficients of p_π and d_π orbitals in the bonding molecular orbital(MO). E_1 and E_2 are the eigen values for the bonding and anti-bonding MO's, respectively. I is the moment of inertia of the ligand atom and ω is the frequency of the bending mode. q_{at} is the atomic field gradient.

Since the d_π hole plays the same role for the EFG at the metal nucleus as the p_π electron for the EFG at the ligand nucleus, this expression can be applied to the present case. It is difficult to estimate the above quantities suitably, but if a low energy lattice vibration ($\omega \approx 20\ \mathrm{cm}^{-1}$) with the nature of a bending mode is assumed, the observed order of Δq can be obtained as follows: Since the electronic state has one hole in the d_π orbital, V is supposed to be 3. For $[H_{12}/(E_2 - E_1)]C_1^0 C_2^0$ a reasonable value 0.1 is used [8]. For I a value $0.84 \cdot 10^{-44}\ \mathrm{kg\,m^2}$ is used. For $(1/2)e^2 Q q_{\mathrm{at}}$ the result of the Fe^{2+} high spin state, 5.6 mm/s [10], is used as the largest value. Then the temperature dependence of QS is estimated to be $0.9 \cdot 10^{-3}$ mm/s K, which is of the same order of magnitude as observed.

At the same time this model can also explain the temperature dependence of the isomer shift. The decrease of the number of 3d electrons with increasing temperature weakens the screening of 4s electrons, elevating the density of 4s electrons at the nucleus. This appears as a linear decrease in the isomer shift such as seen in Table 1.

In the transition metal pentahalides the mechanism due to π bonding also succeeded to assign three groups of halogen NQR lines to three kinds of unequivalent sites [11]. Using this mechanism, the doublets in the Mössbauer spectra may be assigned tentatively as follows: The 4d electrons of the Nb atom are more favorable to forming a π bond with a 4p electron of a Se atom than with a 3d electron of an Fe atom. As a result of the competition about π bonding, Fe(2) atoms are expected to form the strongest π bonding, consequently to exhibit the smallest QS. In this model the doublet B is therefore assigned to an Fe(2) site, which does not conflict with the assignment by Brill et al. [5].

4. Conclusion

In the experiment of Mössbauer effect in $Fe_{1.33}Nb_{2.67}Se_{10}$ a remarkable positive temperature dependence of the QS was found above 250 K. As a possible origin a mechanism due to π bonding is suggested. On the other hand, the spectra could be resolved into two doublets down to lower temperatures than in an other authors' study. This was interpreted as that the short range order still continues to grow even far below the CDW transition temperature.

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