JOURNAL OF SOLID STATE CHEMISTRY **27**, 137–144 (1979)

Lattice Dynamics and Hyperfine Interactions of the Intercalation Compounds: $NbS_2 \cdot Sn$ and $NbS_2 \cdot Sn_{1/3}$

ROLFE H. HERBER AND MOTOMI KATADA

Department of Chemistry, Rutgers—The State University of New Jersey, New Brunswick, New Jersey 08903

Received March 28, 1978; in final form May 15, 1978

The vibrational anisotropy of tin in the two intercalation compounds $NbS_2 \cdot Sn_{1/3}$ and $NbS_2 \cdot Sn$ has been studied over the temperature range $78 \leq T \leq 320$ and $4.2 \leq T \leq 320°K$, respectively, using ^{119}Sn 23.4 Kev gamma resonance spectroscopy. As in the case of the Tantalum homologue, $NbS_2 \cdot Sn_{1/3}$ shows a single resonance maximum indicating a cubic symmetry charge distribution around Sn. The effective Mossbauer (lattice) temperature is 197 ± 5°K. The gamma resonance spectrum of $NbS_2 \cdot Sn$ shows a doublet with a quadrupole hyperfine interaction of 0.954 mm sec^{-1} at 78°K. The intensity ratio of this doublet is temperature dependent and has been analyzed in terms of the Golldanskii–Karyagin Effect to yield a value for $\langle x_\parallel^2 \rangle - \langle x_\perp^2 \rangle = -1.3 \times 10^{18}\ cm^2$ at 300°K. The effective Mössbauer (lattice) temperature for the 1 : 1 compound is 159 ± 5°K calculated from the high temperature limiting slope of the recoil-free fraction temperature dependence. The origin of the isomer shift differences between the TaS_2 and NbS_2 intercalation compounds of tin is discussed.

Because of their unique chemical and solid state properties, intercalation compounds of a number of group Va sulfides have been studied in considerable detail (*1*), albeit sometimes with conflicting interpretation of the available experimental data. In particular, the recent X-ray crystallographic study of the tin intercalation compounds of TaS_2 by Eppinga and Wiegers (*2*) appears to have resolved the apparent discrepancy between the interpretation of the ESCA results of Eppinga *et al.* (*3*) and the Mössbauer effect data of Herber and Davis (*4, 5*) on $TaS_2 \cdot Sn$. In the earlier ^{119}Sn Mössbauer effect study (*4*) of this compound, the doublet observed in the resonance spectrum was interpreted in terms of a quadrupole hyperfine interaction involving the unique tin atom in the layer structure. From the temperature dependence of the intensity asymmetry of this doublet (the Gol'danskii–Karyagin Effect) it was possible to extract a value for the motional anisotropy ($\langle x_\parallel^2 \rangle - \langle x_\perp^2 \rangle$) of the tin atom at 295°K. In addition, the Mössbauer lattice temperature, θ_M, has been reported (*5*) for both $TaS_2 \cdot Sn$ and $TaS_2 \cdot Sn_{1/3}$.

In the present study, these investigations have been extended to the corresponding niobium compounds which the work of Eppinga and Wiegers have shown to be isostructural with the tantalum homologues, and the resulting data have permitted a detailed comparison between the two sets of chalcogenide intercalation solids.

Experimental

$NbS_2 \cdot Sn$ and $NbS_2 \cdot Sn_{1/3}$ were prepared from the stoichiometric mix of high purity commercial Nb, S, and Sn by literature methods. In essence these procedures consist in using evacuated sealed Vycor tubes, and

0022-4596/79/020137-08$02.00/0

heating the reaction mix to 860°C for 48 hr. The solid is cooled, re-ground, then again maintained in an evacuated ampoule at 860°C for one week and cooled slowly. The powders obtained in this manner were characterized by powder X-ray diffraction (Cu K_α radiation) and elemental analysis.

Several unsuccessful attempts were made to prepare large enough single crystals of $NbS_2 \cdot Sn$ to permit an orientational dependence study of the recoil-free fraction. The use of I_2, NH_4Cl and HCl as vapor transport agents, as well as SnI_4 as a volatile source of tin did not yield useable large crystals.

Samples for ^{119}Sn Mössbauer effect studies were prepared by sandwiching thin (~50 to 75 mgm/cm^2) layers of the neat powders between aluminum foil in a copper sample holder which had been provided with a Cd critical X-ray absorber, and mounting this directly onto the cold head of the Cryotip variable constant temperature dewar described earlier (*6*). "Isotropic" $NbS_2 \cdot Sn$ samples were prepared by mixing the neat powder with ~30% Pyrex glass powder and grinding this exhaustively in an agate mortar. The resulting fine particulates were slurried with an appropriate quantity of fast setting epoxy mix, casting the viscous solid into an aluminum foil cup, and allowing the sample to set to a hard, self-supporting disc prior to mounting between aluminum foil thermal shields, as before.

Mössbauer effect measurements over the temperature range $4.2 \leq T \leq 320$°K were effected using the constant acceleration spectrometer described earlier (*6*). Temperature control was adequate to ensure stability to better than ±0.5°C for the time interval necessary to accumulate the Mössbauer data of each temperature point. Data reduction was effected using the least squares matrix inversion program employed in the earlier studies. The raw experimental data were corrected for a geometric (inverse square) effect prior to curve fitting so that in the absence of a resonance effect the transmission is independent of relative source-absorber velocity. Each half of the mirror image spectra was analyzed independently to evaluate the Mössbauer effect parameters.

Spectrometer calibration was effected from the metallic iron magnetic hyperfine interaction data (*7*) obtained using a Pd(^{57}Co) source and an NBS SRM metallic iron absorber at room temperature. All isomer shift data are reported with respect to the $BaSnO_3$ resonance at 295 ± 2°K.

Results and Discussion

The Mössbauer data for $NbS_2 \cdot Sn$ and $NbS_2 \cdot Sn_{1/3}$ are summarized in Table 1, together with data on related samples published earlier. A typical gamma ray resonance spectrum of $NbS_2 \cdot Sn$ is shown in

TABLE I

SUMMARY OF MÖSSBAUER DATA FOR NbS_2 AND TaS_2 INTERCALATION COMPOUNDS WITH TIN

Absorber	IS(78°K) mm sec^{-1}	dIS/dT mm sec^{-1} deg^{-1}	QS(78°K) mm sec^{-1}	$-d \ln \frac{A(T)}{A(78)} \Big/ dT$ deg^{-1}	θ_M deg^{-1}
$TaS_2 \cdot Sn_{1/3}$	3.851	-4.44×10^{-4}	—	3.48×10^{-4}	233 ± 10
$NbS_2 \cdot Sn_{1/3}$	3.681	-2.17×10^{-4}	—	4.61×10^{-3}	197 ± 5
$TaS_2 \cdot Sn^a$	3.13	-3.38×10^{-4}	1.09		176 ± 5
$TaS_2 \cdot Sn$	3.192		1.15	5.50×10^{-3}	185 ± 10
$NbS_2 \cdot Sn$	3.134	-3.4×10^{-4}	0.954	7.03×10^{-3}	159 ± 5

[a] singe crystal sample

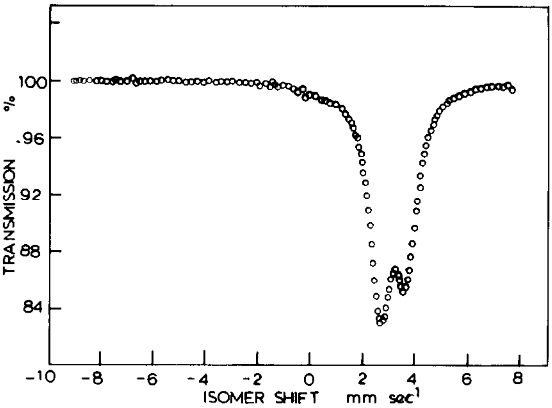

FIG. 1. ^{119}Sn Mössbauer spectrum of NbS$_2$·Sn at 78°K. The isomer shift scale is relative to the center of a BaSnO$_3$ absorber spectrum at 295 ± 2°K using the same source as that used in the sample compound spectra.

Fig. 1, while the corresponding spectrum of NbS$_2$·Sn$_{1/3}$ is shown in Fig. 2. It will be immediately obvious from these figures that the niobium compounds give results very similar to those observed for the tantalum homologues; that is, in the Nb : Sn = 3 : 1 compound the tin atom occupies a site having cubic charge symmetry, and thus giving rise to a single, unbroadened resonance maximum, while in the 1 : 1 compound the ^{119}Sn resonance is split into a well resolved doublet resulting from a quadrupole hyperfine interaction at the tin atom lattice site. The value of the isomer shift parameter is such that the tin atom can be considered to be formally in the Sn^{2+} ([Kr core]$4d^{10}5s^2$) state in both the 3 : 1 and the 1 : 1 compounds.

NbS$_2$·Sn$_{1/3}$. The isomer shift for the singlet resonance observed in this compound at liquid nitrogen temperature is shifted by −0.17 mm sec^{-1} from the corresponding value in TaS$_2$·Sn$_{1/3}$. Using the observation that the isomer shift in ^{119}Sn spectra increases by ~2.5 mm sec^{-1} per unit increase in 5s electron population leads to a decrease of ~7% of a 5s electron in NbS$_2$·Sn$_{1/3}$ compared to TaS$_2$·Sn$_{1/3}$. The bond ionicities of group V dichalcogens have been discussed by Madhukar (*8*) who has shown that the metal–sulfur bond in NbS$_2$ is more covalent

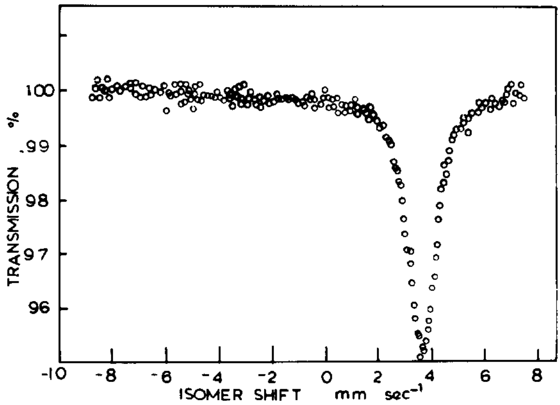

FIG. 2. ^{119}Sn Mössbauer spectrum of NbS$_2$·Sn$_{1/3}$ at 78°K. See caption for Fig. 1.

(by ~4%) than the corresponding bond in TaS_2. The photoelectron spectrum of $TaS_2 \cdot Sn_{1/3}$ shows that the electron donation is from the Sn to Ta as evidenced by the increase in occupation of the lowest 5*d* orbital of Ta. Thus on this basis it might have been inferred that there should be more electron transfer in the case of the Sn–Ta interaction than in the case of the Sn–Nb bond, in contrast to what is observed experimentally. The observed isomer shift difference can, however, be understood on the basis of the difference in the bond character of the Sn–Ta and Sn–Nb bond itself. In the former the tin 5*s*, 5*p* electrons overlap with a Ta 5*d* orbital, whereas in the latter the overlap is with a Nb 4*d* orbital. The latter is expected to have a greater covalent character than the former and hence be more effective in reducing the 5*s* electron density around the tin atom, compared to the bonding interaction in the tantalum homologue. The implications of this reasoning are that the tin atom is bound to the NbS_2 layer structure by *bona fide* chemical bonding interactions, rather than by simple van der Waals forces within the chalcogen atom planes of the layer compound.

In this context it is interesting to note that a comparable shift to lower values is observed in the isomer shift data for $NbS_2 \cdot Sn$ relative to $TaS_2 \cdot Sn$. In these compounds, the presence of a quadrupole hyperfine interaction can be taken as unambiguous evidence for a chemical bonding interaction between the intercalated atom and the host matrix.

The temperature dependence of the isomer shift parameter, $dIS/dT = -2.2 \times 10^{-4}$ mm sec^{-1} deg^{-1} for $NbS_2 \cdot Sn_{1/3}$ is somewhat smaller than that observed in the tantalum homologue, or the classical value of -3.5×10^{-4} mm sec^{-1} deg^{-1} calculated from the first term of the Debye model high temperature Thirring expansion, again indicative of increased chemical bonding between the intercalated atom and the host matrix. Such bonding has the effect of increasing the effective mass of the moiety undergoing the second order Doppler shift and thus decreases the temperature dependence of the IS parameter.

The temperature dependence of the recoil-free fraction for the ^{119}Sn Mössbauer transition in $NbS_2 \cdot Sn_{1/3}$ can be extracted from the temperature dependence of the area under the resonance curve, and these data are summarized in Fig. 3. The data at high ($T > 250$°K) temperatures show evidence for considerable motional anharmonicity, but the data lying in the temperature interval $78 < T < 225$°K are well fit by a linear expression of the form $\ln A(T)/A(78) = -4.608 \times 10^{-3}\, T + 0.3611$, with a least squares correlation coefficient of unity for the six data points. The coefficient of the temperature dependent term can be used to calculate a value of the Mössbauer

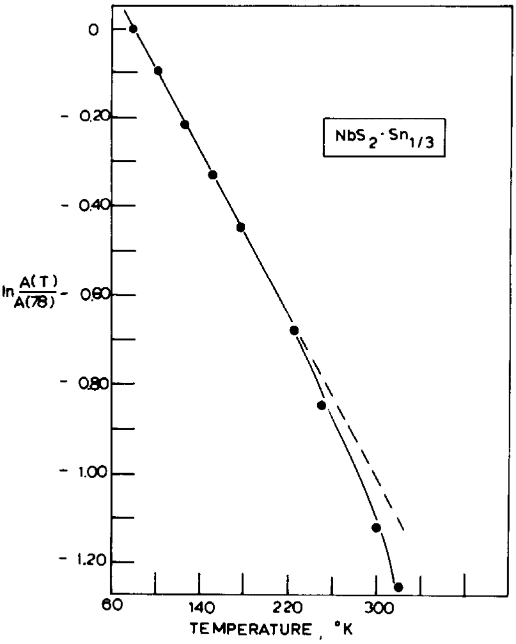

FIG. 3. Temperature dependence of the area under the resonance curve (normalized to the 78°K point) for $NbS_2 \cdot Sn_{1/3}$. The straight line is a linear least squares fit to the data in the interval $78 \leq T \leq 225$°K.

lattice temperature θ_M, from the relationship

$$\frac{-d\ln f}{dT}=-d\ln\frac{[A(T)/A(78)]}{dT}=\frac{3E_\gamma^2}{Mc^2k\theta_M^2} \tag{1}$$

if the assumption is made (*vide supra*) that the effective vibrating mass, M, is the mass of a "bare" tin atom. Under this (admittedly questionable) assumption, the observed temperature dependence of the normalized area, $\ln[A(T)/A(78)]$ implies a Mössbauer temperature, θ_M, of 197 ± 5°K. The lattice temperature reported (*5*) for $TaS_2{\cdot}Sn_{1/3}$ is 233 ± 10°K.

The effective vibrating mass, M, can be extracted from the temperature dependence of the isomer shift; that is

$$\frac{dIS}{dT}=-\frac{3}{2}\frac{E_\gamma k}{Mc^2} \tag{2}$$

combining (1) and (2) leads to an expression of the form

$$\theta_M=\frac{(2E_\gamma)^{1/2}}{k}\left[\frac{dIS/dt}{d\ln A(T)/A(78)/dT}\right]^{1/2} \tag{3}$$

$$=7.155\times10^2\left[\frac{dIS/dT}{d\ln A(T)/A(78)/dT}\right]^{1/2}. \tag{3'}$$

Using the data referred to above for $NbS_2{\cdot}Sn_{1/3}$ leads to a value of $\theta_M=155\pm5°K$ in the high temperature ($T>\theta/2$) limit, and reflects the increase in the effective vibrating mass of the tin atom due to chemical bonding effects within the intercalation compound structure.

$NbS_2{\cdot}Sn$. As shown in Fig. 1, the ^{119}Sn Mössbauer spectrum of this compound shows a pattern indicative of a quadrupole hyperfine interaction in consonance with the earlier date (*4, 5*) for the corresponding tantalum compound. The isomer shift at 78°K is ~3.13 mm $\sec^{-1}$ with respect to $BaSnO_3$, and is thus shifted by ~−0.03 mm $\sec^{-1}$ with respect to $TaS_2{\cdot}Sn$. This difference is probably not significant within the experimental errors of the present study. The temperature dependence of the recoil-free fraction over the range $4.2\le T\le 320$°K is summarized in Fig. 4. In the high temperature limit ($T\ge\theta/2$), $d\ln A(T)/A(78)/dT=-7.028+10^{-3}\,\deg^{-1}$ with a correlation coefficient of 0.989 for a linear regression analysis of 19 data points. As before, making the assumption that the effective vibrating mass in equation (1) is that of a bare tin atom in the $NbS_2{\cdot}Sn$ intercalate leads to a value of $\theta_M=159\pm5$°K.

The quadrupole splitting at liquid nitrogen temperature is 0.954 ± 0.010 mm $\sec^{-1}$ and is thus ~15% smaller than it is in $TaS_2{\cdot}Sn$. As was observed in the case of the latter compound, the relative intensity of the two components of the quadrupole doublet in $NbS_2{\cdot}Sn$ is temperature dependent, indicative of an anisotropy of the recoil-free

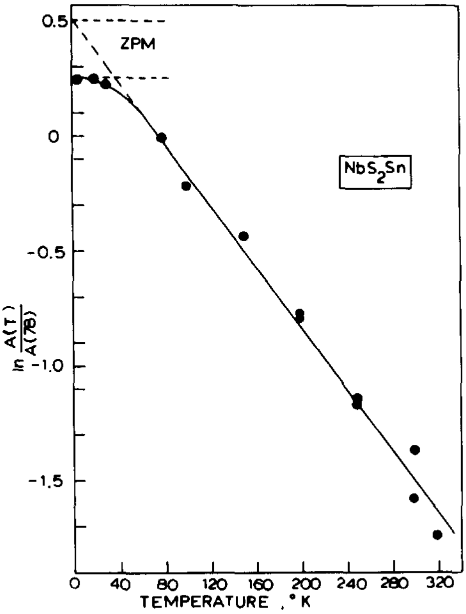

FIG. 4. Temperature dependence of the area under the resonance curve (normalized to the 78°K point) for $NbS_2{\cdot}Sn$. The straight line is a linear least squares fit to the data in the interval $78\le T\le320$°K. The effect of zero point motion (ZPM) is evident in the low temperature data.

fraction (Gol'danskii–Karyagin Effect) (*9*). It is well known (*10*) that preferential crystal orientation—especially in the case of solids which assume plate-like or needle-shaped habits—will also lead to an asymmetry in the relative intensity of the two components of a quadrupole doublet, although this asymmetry is normally temperature independent. As discussed above, several attempts were made to prepare "isotropic" $NbS_2{\cdot}Sn$ by a combination of grinding the sample with Pyrex glass powder and suspension of the resulting microcrystals in epoxy cement.

Examination of these samples by ^{119}Sn Mössbauer spectroscopy down to 4.2°K showed that even at liquid helium temperature, a noticeable asymmetry in the intensity of the quadrupole doublet remained. A major contribution to this asymmetry is assumed to arise from residual crystal orientation effects, $R(0)$, and this temperature independent factor has been corrected for in the subsequent data analysis. An additional small contribution to the asymmetry may arise from the presence of small amounts of unreacted metallic tin in the sample. The isomer shift of β-Sn at room temperature is $2.55 \pm 0.01\ \mathrm{mm\ sec^{-1}}$ with respect to $BaSnO_3$, and hence any resonance due to this type of tin atom would not be resolved from the component of the quadrupole doublet at an isomer shift of $\sim 2.66\ \mathrm{mm\ sec^{-1}}$ in the $NbS_2{\cdot}Sn$ spectra, nor would the power X-ray diffraction data show the presence of a few percent of metallic tin. Any such contribution to the intensity asymmetry—which would have a strong temperature dependence—has been ignored in the data analysis.

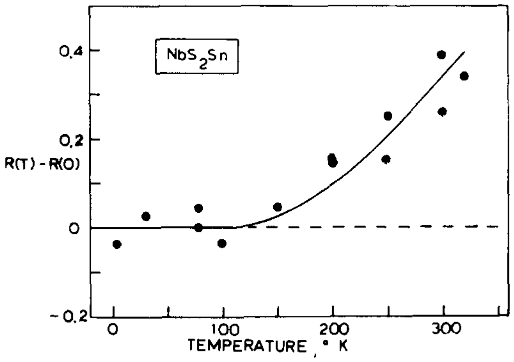

FIG. 5. Net temperature dependence of the intensity asymmetry ratio for $NbS_2{\cdot}Sn$ due to anisotropy of the motional amplitude. The data have been corrected for temperature independent crystal orientation effects as discussed in the text.

The net temperature dependent intensity asymmetry for $NbS_2{\cdot}Sn$ is summarized in Fig. 5 in which the quantity plotted in the vertical direction is $R^{\circ}(T) = R(T) - R(0)$. Here, R is the ratio of the area under the positive velocity component of the Mössbauer doublet to that under the negative velocity component, taking the spectrum centroid as the reference point; that is,

$$R(T) = A_{+}(T)/A_{-}(T).$$

The intensity ratio observed in a Mössbauer spectrum due to the Gol'danskii–Karyagin effect has been given expressly in terms of the mean square vibrational amplitudes parallel and perpendicular to the symmetry axis by Gol'danskii and Makarov (*11*) in the form

$$A = \frac{\int_0^{\pi} \exp\{-(1/\lambda\!\!\!^{-}{}^2)\,[\langle x_{\parallel}^2\rangle - \langle x_{\perp}^2\rangle]\cos^2\theta\} \times (1+\cos^2\theta)\sin\theta\, d\theta}{\int_0^{\pi} \exp\{-(1/\lambda\!\!\!^{-}{}^2)\,[\langle x_{\parallel}^2\rangle - \langle x_{\perp}^2\rangle]\cos^2\theta\} \times (\frac{5}{3}-\cos^2\theta)\sin\theta\, d\theta}$$
$$= M_{\pi}/M_{\sigma}.$$

The relationship between $R(T)$ and $A(T)$ depends on the shape of the electric charge distribution about the molecular symmetry axis passing through the Mössbauer active atom. In the case of $NbS_2{\cdot}Sn$, the molecular symmetry axis is taken to be the crystallographic c-axis, that is, the axis normal to the sulfur atom layers and passing through the tin atom. As Eppinga and Wiegers (*2*) have shown, the coordination of the tin in this structure is somewhat unusual: each Sn atom is linearly coordinated by two sulfur atoms of the NbS_2 structure adjacent to the (hexagonal) Sn layers. A similar nearest neighbor arrangement of sulfur atoms with respect to Sn has been reported (*12, 13*) for $SnMo_6S_8$ in which the tin has 8 neighboring sulfur atoms; two in linear coordination at a distance of 2.8 Å, the other six at a distance of about 3.1 Å, compared to the corresponding values of 2.78 Å and 3.3 Å calculated by Eppinga and Wiegers (2) for $NbS_2 \cdot Sn$ and $TaS_2 \cdot Sn$. It is assumed that the electrons of the intercalated Sn atoms are donated to the $NbS_2d_{z^2}$ band, one electron from each atom being sufficient to fill this band. This electron transfer leaves the tin atom with effectively one 5*s* electron, and is thus consistent with the isomer shift value referred to above (see also Table I) and close to the value observed for metallic (β) tin. Moreover, the transfer of an electron from Sn to S in the (linear) chain array of atoms in the structure gives rise to a charge distribution around the tin atom which can be described as being oblate (with respect to the crystallographic *c*-axis) and hence (*14*) the measured intensity asymmetry, $R°(T)$ will be inversely proportional to the ratio of the $\pi(\pm 3/2 \leftrightarrow \pm 1/2)$ to the $\sigma(\pm 1/2 \leftrightarrow \pm 1/2)$ transition. The solution of the integral equation given by Gol'danskii and Makarov has been summarized graphically by Flinn, Ruby and Kehl (*15*), and from their data the vibrational anisotropy of the tin atom in $NbS_2 \cdot Sn$ at 300°K is calculated to be $\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle \approx -1.3 \times 10^{-18}\ \mathrm{cm}^2$. This result, that the tin atom executes a larger mean square amplitude of motion perpendicular to the crystallographic *c*-axis (within the Sn layers) than parallel to this axis, is in agreement with the earlier data (*4*) on the isostructural $TaS_2 \cdot Sn$ as well as the interpretation of the X-ray diffraction data of Eppinga and Wiegers (*2*).

As noted above, it has not proven possible so far to obtain large enough single crystals of $NbS_2 \cdot Sn$ to effect an oriented single crystal study of this compound as was carried out (*5*) with the $TaS_2 \cdot Sn$ isomorph. However, the present results, together with those of the X-ray study referred to above leave little doubt that there is a single type of tin atom in the niobium sulfide intercalate described in these investigations. The vibrational anisotropy of the intercalated tin atom in both $TaS_2 \cdot Sn$ and $NbS_2 \cdot Sn$ is a microscopic manifestation of the anisotropy of the bulk properties of these layer structure compounds.

Acknowledgments

This research was supported in part by the National Science Foundation under grant DMR-7600139 and by a grant from the Rutgers Center for Computer and Information Services. This support is herewith gratefully acknowledged. The authors are also indebted to Dr. F. J. DiSalvo for numerous helpful discussions and to B. Toby and Dr. M. F. Leahy for assistance with some of the computer routines used in the data reduction procedures.

References

1. F. R. GAMBLE, J. H. OSIECKI, M. CAIS, R. PISHARODY, F. J. DISALVO, AND T. H. GEBALLE, *Science* **174**, 493 (1971); F. R. GAMBLE, J. H. OSIECKI, AND F. J. DISALVO, *J. Chem. Phys.* **55**, 3525 (1971); F. J. DISALVO, G. W. HULL, JR., L. H. SCHWARTZ, J. M. VOORHOEVE, AND J. V. WASZCZAK, *J. Chem. Phys.* **59**, 1922 (1973).
2. R. EPPINGA AND G. A. WIEGERS, *Mat. Res. Bull.* **12**, 1057 (1977).
3. R. EPPINGA, G. A. SAWATZKY, C. HAAS, AND C. F. VAN BRUGGEN, *J. Phys. Chem.* **9**, 3371 (1975).
4. R. H. HERBER AND R. F. DAVIS, *J. Chem. Phys.* **63**, 3668 (1975).
5. R. H. HERBER AND R. F. DAVIS, *J. Chem. Phys.* **65**, 3773 (1976).
6. A. J. REIN AND R. H. HERBER, *J. Chem. Phys.* **63**, 1021 (1975) and references therein.
7. J. J. SPIJKERMAN, J. R. DEVOE, AND J. C. TRAVIS, Nat. Bur. Stand. (U.S.) Spec. Pub. 260-20 (1970); R. H. HERBER *in* "Mössbauer Effect Methodology," Vol. 6; I. J. Gruverman, Ed., Plenum Press, New York, 1971.
8. A. MADHUKAR, *Solid State Communic.* **16**, 383 (1975).
9. V. I. GOL'DANSKII, E. F. MAKAROV, AND V. V. KHRAPOV, *Phys. Lett.* **3**, 334 (1963); S. V. KARYAGIN, *Dokl. Akad. Nauk SSSR*, **148**, 1102 (1963).

10. H. D. PFANNES AND V. GONSER, *J. Appl. Phys.* **1**, 93 (1973): U. GONSER AND H. D. PFANNES, *J. Physique* (*Paris*) **C6**, 113 (1974).

11. V. I. GOL'DANSKII AND E. F. MAKAROV *in* "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Eds., Academic Press, New York, 1968.

12. J. BOLZ, J. HAUCK, AND F. POBELL, *Z. Phys.* **B25**, 351 (1976).

13. C. W. KIMBALL, L. WEBER, G. VAN LANDHUYT, F. Y. FRADIN, B. D. DUNLAP, AND G. K. SHENOY, *Phys. Rev. Lett.* **36**, 412 (1976).

14. R. H. HERBER *in* "Mössbauer Spectroscopy and its Applications," IAEA, Vienna 1972, pp. 267ff.

15. P. S. FLINN, S. L. RUBY, AND W. L. KEHL, *Science* **143**, 1434 (1964).