PHYSICAL REVIEW B VOLUME 36, NUMBER 16 1 DECEMBER 1987

Theoretical explanation of zero-field splitting and its pressure, stress, and temperature dependence in $NiSiF_6\cdot 6H_2O$

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(Received 18 May 1987)

When the contribution from splitting due to the electron-phonon interaction (SEPI) is taken into consideration, the zero-field splitting D and its pressure, stress, and temperature dependence in $NiSiF_6\cdot 6H_2O$ can be explained reasonably from the combination of macroscopic thermodynamic analysis and microscopic crystal-field theory. It is shown that the SEPI cannot be ignored in the calculation of the parameter D at room temperature, since D strongly depends on the temperature.

The EPR parameter D and its pressure, stress, and temperature dependence in $NiSiF_6\cdot 6H_2O$ were measured several decades ago,[1-3] but there is still no satisfactory theoretical explanation for all of them. Walsh[3] used a static, ionic model to explain these findings. Because the splitting due to the electron-phonon interaction (SEPI) was not taken into consideration, the polar-angle deformation $(\alpha-\alpha_0)$ in this model was not only inconsistent with the experimental results, but also with the thermodynamic analysis given by him (see Table I). The pressure and stress dependence of the parameter D also were not explained quantitatively. Recently, Xiong, Bai, and Zhao[4] have made some progress on this problem. They first established the state equation of $NiSiF_6\cdot 6H_2O$ from experimental results on the pressure dependence of the zero-field splitting D, and used the approximate self-consistent field (SCF) d orbital of Ni^{2+} and the state equation obtained above to explain the pressure dependence of D from microscopic crystal-field theory. However, there are three unresolved points in their work: (1) The calculational result for the crystalline parameter α $(=54.89^\circ)$ given by them from the x-ray data[5] is incorrect; the correct value of the parameter α, according to my calculation, should be $55.09^\circ \pm 0.07^\circ$ from the same x-ray data. So the values of the parameter D and its hydrostatic pressure dependence calculated by them from the incorrect crystalline parameter raise doubts. The agreement between the above calculation values and the experimental results given by them is also unreliable. (2) The coefficients of the state equation were not given, and so we could not compare then with the compressibilities which were measured decades ago.[3] If the coefficients are calculated from the method given in their paper, it can be found that they do not fit with the experimental data. (3) When $P=6200$ kg/cm^2 the value of D vanishes and the authors of Ref. 4 thought it meant that the site symmetry of Ni^{2+} is cubic (this shows that dynamic effects on the splitting of D were also not taken into consideration by them). This conclusion may be regarded as correct in most cases. However, in cases when the parameter D strongly depends on the temperature, it is no longer reliable, because the zero-field splitting is due to both a static crystalline field (D_s) and a dynamic phonon contribution (D_p), i.e., $D=D_s+D_p$. $D=0$ only means the general symmetry is cubic, but, when the SEPI is large, the general symmetry should be different from the static symmetry.[6] In fact, the temperature dependence of D in $NiSiF_6\cdot 6H_2O$ is so strong that it can be used as a thermometer.[7] In addition, from the experimental data of crystalline parameters[5] (polar angle $\alpha=55.09^\circ \pm 0.07^\circ$) and compressibilities[3] $[(\partial \ln\alpha/\partial P)_T = -0.635\times 10^{-6}\ (\text{kg/cm}^2)^{-1}]$ of $NiSiF_6\cdot 6H_2O$, we can find that only when $P=9800$ kg/cm^2 will the site symmetry be cubic $(\alpha_0=54.736^\circ)$, while if $P=6200$ kg/cm^2, then $\alpha=54.863^\circ$, which would predict $D_s\neq 0$. For the above reasons, the contribution from the SEPI must be taken into consideration in calculating the experimental data of the zero-field splitting in $NiSiF_6\cdot 6H_2O$.

TABLE I. Comparison of $\alpha-\alpha_0$ [experimental value $=0.35 \pm 0.07$ (from Ref. 7)].

$\alpha-\alpha_0$ (deg)	Walsh (Ref. 3)	This work
Thermodynamic theory	0.2	0.348
Crystal-field theory	0.6	0.341

In this paper we will introduce the contribution from the SEPI to explain the zero-field splitting and its pressure, stress, and temperature dependence in $NiSiF_6\cdot 6H_2O$ at room temperature. The results are consistent with those obtained from the experiments.

In $NiSiF_6\cdot 6H_2O$ crystals, the Ni^{2+} ions are surrounded by an oxygen (or water) octahedron with a weak trigonal deformation. Using the "quasi-intermediate-field" method and fourth-order perturbation theory,[8] the axial parameter D of d^8 ions in a trigonal crystal field is

$$D=\frac{\xi_d^2 v}{2W_1}-\frac{\xi_d^2 v}{2W_2}-\frac{3\sqrt{2}\xi_d^2 v'}{2W_1W_3}+\frac{3\sqrt{2}\xi_d^2 v'}{2W_2W_3}-\frac{18\sqrt{2}B\xi_d^2 v'}{W_1W_3W_4}-\frac{18\sqrt{2}B\xi_d^2 v'}{W_2W_3W_4}+\frac{6\sqrt{2}B\xi_d^2 v'}{W_2W_3W_5}+\frac{6\sqrt{2}B\xi_d^2 v'}{W_2^2W_5}, \tag{1}$$

where W_i denotes the energy difference between the $^3A_2$ ground state and the corresponding excited level in O_h approximation, and v and v' are the trigonal-field parameters. From the point-charge dipole model, v and v' are

$$v=\tfrac{18}{7}(3\cos^2\alpha-1)\frac{e^2}{R^3}\left(1+\frac{3\mu}{eR}\right)\langle r^2\rangle+\tfrac{10}{21}(35\cos^4\alpha-30\cos^2\alpha+3)\frac{e^2}{R^5}\left(1+\frac{5\mu}{eR}\right)\langle r^4\rangle$$
$$+\frac{10\sqrt{2}}{3}\sin^3\alpha\cos\alpha\frac{e^2}{R^5}\left(1+\frac{5\mu}{eR}\right)\langle r^4\rangle\ , \qquad (2)$$

$$v'=-\frac{6\sqrt{2}}{7}(3\cos^2\alpha-1)\frac{e^2}{R^3}\left(1+\frac{3\mu}{eR}\right)\langle r^2\rangle+\frac{5\sqrt{2}}{4}(35\cos^4\alpha-30\cos^2\alpha+3)\frac{e^2}{R^5}$$
$$\times\left(1+\frac{5\mu}{eR}\right)\langle r^4\rangle+\tfrac{5}{3}\sin^3\alpha\cos\alpha\frac{e^2}{R^5}\left(1+\frac{5\mu}{eR}\right)\langle r^4\rangle\ . \qquad (3)$$

Utilizing the SCF d orbital of Ni^{2+} ions[4]

$$R_d(r)=0.73948[O(5.511)]+0.50000[O(1.5746)]\ , \qquad (4)$$

where O denotes a Slater orbital we have[9]

$$B_0=1208\ \text{cm}^{-1},\ C_0=4459\ \text{cm}^{-1},\ \xi_{d0}=650\ \text{cm}^{-1}\ ,$$
$$\langle r^2\rangle_0=1.8904\ \text{a.u.},\ \langle r^4\rangle_0=13.4043\ \text{a.u.}\ . \qquad (5)$$

By introducing the average covalency parameter N,[10] then

$$B=N^4B_0,\ C=N^4C_0,\ \xi_d=N^2\xi_{d0},\ \langle r^K\rangle=N^2\langle r^K\rangle_0\ . \qquad (6)$$

From the optical absorption spectra of $NiSiF_6\cdot 6H_2O$,[11] we get $N=0.9$, $\mu=0.02\ e$Å. Substituting these data and x-ray data of $NiSiF_6\cdot 6H_2O$ [$R=2.048$ Å, $\alpha=55.08°$] (Ref. 7) into the above formulas, we obtain

$$D_s=-0.81\ \text{cm}^{-1}\ . \qquad (7)$$

Comparing D_s with the observed value of D [$D=-0.52\ \text{cm}^{-1}$ (Ref. 3)], we find

$$D_p=0.29\ \text{cm}^{-1}\ . \qquad (8)$$

It is clear that the SEPI is not small and must be taken into consideration.

In order to show the reasonableness of this idea, the pressure, stress, and temperature dependence of D are studied on this basis.

Under pressure,

$$R(P)=R\left[1+\left(\frac{\partial\ln R}{\partial P}\right)_T P\right]\ , \qquad (9)$$

$$\alpha(P)=\alpha\left[1+\left(\frac{\partial\ln\alpha}{\partial P}\right)_T P\right]\ , \qquad (10)$$

with[3]

$$\left(\frac{\partial\ln R}{\partial P}\right)_T=\left(\frac{\partial\ln R_\perp}{\partial P}\right)_T\sin^2\alpha+\left(\frac{\partial\ln R_\parallel}{\partial P}\right)_T\cos^2\alpha$$
$$=-1.77\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ , \qquad (11)$$

$$\left(\frac{\partial\ln\alpha}{\partial P}\right)_T=\frac{\sin2\alpha}{2\alpha}\left[\left(\frac{\partial\ln R_\perp}{\partial P}\right)_T-\left(\frac{\partial\ln R_\parallel}{\partial P}\right)_T\right]$$
$$=-0.635\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ . \qquad (12)$$

Using Eqs. (9)-(12) and (1), we obtain

$$\left(\frac{\partial D}{\partial P}\right)_T=0.865\times10^{-4}\ \text{cm}^{-1}(\text{kg/cm}^2)\ . \qquad (13)$$

The result agrees well with the experimental value [$(\partial D/\partial P)_T=0.834\times10^{-4}\ \text{cm}^{-1}/(\text{kg/cm}^2)$ (Ref. 3)].

In the case of uniaxial stress, no values of $(\partial\ln R_\parallel/\partial U)_T$ and $(\partial\ln R_\perp/\partial U)_T$ were given experimentally. Walsh[3] gave estimates but no reasons for them. Here we use

$$\left(\frac{\partial\ln R_\parallel}{\partial P}\right)_T=-(S_{33}+2S_{13}),\quad \left(\frac{\partial\ln R_\perp}{\partial U}\right)_T=-S_{13}\ , \qquad (14)$$

then

$$\left(\frac{\partial\ln R_\parallel}{\partial U}\right)_T=-S_{33}=\left(\frac{\partial\ln R_\parallel}{\partial P}\right)_T-2\left(\frac{\partial\ln R_\perp}{\partial U}\right)_T\ . \qquad (15)$$

There is only one variable related to the change of D with stress, so we can determine it from the experimental value of the stress dependence of D:

$$\left(\frac{\partial\ln R_\perp}{\partial U}\right)_T=0.580\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ , \qquad (16)$$

and

$$\left(\frac{\partial\ln R_\parallel}{\partial U}\right)_T=-2.06\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ . \qquad (17)$$

They are very similar to the estimates:

$$\left(\frac{\partial\ln R_\perp}{\partial U}\right)_T=0.55\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ ,$$
$$\left(\frac{\partial\ln R_\parallel}{\partial U}\right)_T=-2.0\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ .$$

Applying equations similar to Eqs. (11) and (12) gives

$$\left(\frac{\partial\ln R}{\partial U}\right)_T=-0.285\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ , \qquad (18)$$

$$\left(\frac{\partial\ln\alpha}{\partial U}\right)_T=1.29\times10^{-6}\ (\text{kg/cm}^2)^{-1}\ . \qquad (19)$$

For macroscopic thermodynamic analysis we have

$$\left(\frac{\partial D}{\partial T}\right)_P=\left(\frac{\partial D}{\ln R}\right)_{\alpha,T}\left(\frac{\partial \ln R}{\partial T}\right)_P+\left(\frac{\partial D}{\partial \ln \alpha}\right)_{R,T}\left(\frac{\partial \ln \alpha}{\partial T}\right)_P+\left(\frac{\partial D}{\partial T}\right)_{R,\alpha}, \tag{20}$$

$$\left(\frac{\partial D}{\partial P}\right)_T=\left(\frac{\partial D}{\partial \ln R}\right)_{\alpha,T}\left(\frac{\partial \ln R}{\partial P}\right)_T+\left(\frac{\partial D}{\partial \ln \alpha}\right)_{R,T}\left(\frac{\partial \ln \alpha}{\partial P}\right)_T, \tag{21}$$

$$\left(\frac{\partial D}{\partial U}\right)_T=\left(\frac{\partial D}{\partial \ln R}\right)_{\alpha,T}\left(\frac{\partial \ln R}{\partial U}\right)_T+\left(\frac{\partial D}{\partial \ln \alpha}\right)_{R,T}\left(\frac{\partial \ln \alpha}{\partial U}\right)_T. \tag{22}$$

Substituting Eqs. (11) and (12), and (18) and (19) into Eqs. (21) and (22) we obtain

$$\left(\frac{\partial D}{\partial \ln \alpha}\right)_{R,T}=-128\,\mathrm{cm}^{-1}, \tag{23}$$

$$\left(\frac{\partial D}{\partial \ln R}\right)_{\alpha,T}=-1.4\,\mathrm{cm}^{-1}. \tag{24}$$

From (1), we can calculate the partial derivatives of D and obtain

$$\left(\frac{\partial D}{\partial \ln \alpha}\right)_{R,T}=-131\,\mathrm{cm}^{-1}, \tag{25}$$

$$\left(\frac{\partial D}{\partial \ln R}\right)_{\alpha,T}=-6.8\,\mathrm{cm}^{-1}. \tag{26}$$

It can be seen that for $(\partial D/\partial \ln\alpha)_{R,T}$, the result of macroscopic thermodynamic analysis is very consistent with that of microscopic crystal-field theory, and for $(\partial D/\partial \ln R)_{\alpha,T}$, the difference between them is slightly larger. Considering that $(\partial D/\partial \ln\alpha)_{R,T} \gg (\partial D/\partial \ln R)_{\alpha,T}$, the very small measurement errors of $(\partial \ln\alpha/\partial P)_{R,T}$, $(\partial \ln\alpha/\partial U)_{R,T}$, $(\partial D/\partial P)_T$, or $(\partial D/\partial U)_T$ can lead to greater changes of $(\partial D/\partial \ln R)_{\alpha,T}$, the difference may be understood.

According to Vasyukov, Lukin, and Tsintsadze,[12] the parameter D may be expanded to first order in $(\alpha-\alpha_0)$:

$$D_s=(\alpha-\alpha_0)\left(\frac{\partial D}{\partial \alpha}\right)_{\alpha=\alpha_0}, \tag{27}$$

where $\alpha_0=54.736°$ (the polar angle for cubic symmetry).

When the difference between α and α_0 is very small, we have

$$\left(\frac{\partial D}{\partial \alpha}\right)_{\alpha=\alpha_0}\approx\left(\frac{\partial D}{\partial \alpha}\right)_{\alpha}\approx\frac{1}{\alpha}\left(\frac{\partial D}{\partial \ln \alpha}\right)_{R,T}.$$

The value of $\alpha-\alpha_0$ can be calculated from Eq. (27).

A comparison of the values of $\alpha-\alpha_0$ obtained from thermodynamic analysis and crystal-field theory in this work with those of Walsh[3] is given in Table I. Both of the values in this work are almost the same as the experimental data, but in Walsh, they are not only inconsistent with each other, but also different from that of experiment.

When $P=6200$ kg/cm^2, $\alpha(P)=\alpha[1+(\partial \ln\alpha/\partial P)_{R,T}P]=54.863°$. From Eq. (27), we obtain $D_s\approx-0.29\,\mathrm{cm}^{-1}$, so that

$$D=D_s+D_p=0\,. \tag{28}$$

It explains that D vanishes when $P=6200$ kg/cm^2.

From $(\partial D/\partial \ln R)_{\alpha,T}=-6.8\,\mathrm{cm}^{-1}$ and $D_s=-0.81\,\mathrm{cm}^{-1}$ a simple calculation shows that $|D_s|\propto R^8$. The result is in good agreement with that of Walsh[3] obtained from the static, ionic model.

Substituting the thermal expansion coefficients into Eqs. (1) and (20), we find that the change of D with temperature due to thermal expansion is $38\times10^{-4}\,\mathrm{cm}^{-1}/\mathrm{K}$ from both thermodynamic and crystal-field methods. Therefore, the change in D caused by thermal vibrations is $-57.5\times10^{-4}\,\mathrm{cm}^{-1}/\mathrm{K}$ [because $(\partial D/\partial T)_P=-19.5\times10^{-4}\,\mathrm{cm}^{-1}/\mathrm{K}$ (Ref. 3)]. This shows that the lattice-vibration contribution to the change of D with the temperature is opposite in sign and larger in magnitude than the static geometrical contribution at room temperature. So the SEPI must be taken into consideration in calculating the value of D.

From what was mentioned above, the zero-field splitting D and its pressure, stress, and temperature dependence in $\mathrm{NiSiF_6\cdot 6H_2O}$ can be explained reasonably when the contribution of lattice vibrations to D is taken into consideration. This is, to my knowledge, the first interpretation of all the three dependencies from a combination of macroscopic thermodynamic and microscopic crystal-field theory. The method should be effective for other similar materials.

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