Magnetic Susceptibility due to the Tight Binding Band Structure and RKKY Interactions in Rare Earth Magnetic Semiconductor

Akira NARITA

(Received on 31 October, 1986)

1. Introduction

The Gd compounds are the typical materials for which the magnetism can be described only by the RKKY interaction. We have chosen the Gd monopnictides (GdX : X = N, P, As, Sb,) and calculated the RKKY interaction $J(\mathbf{R}_n)$ using the simplified band structure [1—4], because they crystallize in the simple NaCl type structure and their band structures have the common properties to other rare earth monopnictides and monochalcogenides [5—7]. The theoretical results have been compared with the experiments. The agreement between the theory and the experiments is good for GdN but bad for other pnictides for which the theory gave the ferromagnetic ordering while the experiments show the antiferromagnet [13, 18]. In order to develope the theory further so as to explain the experiments more completely, we must refine the approximation for the band structure. For this purpose, it is convienient to use the band structure due to the tight binding model. We will calculate numerically the susceptibility $\chi(\mathbf{Q})$ using its band structure, because the calculation of it is easier than that of $J(\mathbf{R}_n)$ and it gives the direct information about the spin ordering. In this note, I consider the numerical calculation method of $\chi(\mathbf{Q})$, including the treatment of the symmetrical property of matrix element, and show its numerical result for a semiconducting GdN as the first step in the sequence of these calculations.

2. Symmetry of the matrix element

In the tight binding model [8—10], the 5d electron on Gd sites and the p electron on pnictogen sites are treated as the band electron. The Bloch function $\phi_{\nu\mathbf{k}}(\mathbf{r})$ with the band number ν in this model can be constructed in the form,

$$\phi_{\nu\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n} \sum_{\alpha} \exp(i\mathbf{k}\mathbf{R}_n)\, B_{\nu\mathbf{k}\alpha}\, \phi_\alpha(\mathbf{r}-\mathbf{R}_n), \tag{1}$$

where $\phi_\alpha(\mathbf{r}-\mathbf{R}_n)$ is the atomic wave functions with the cubic symmetry on the site $\mathbf{R}_n$, and it has the d character on Gd sites and the p character on pnictogen sites, N is the number of Gd atom per unit volume, and $B_{\nu\mathbf{k}\alpha}$ is the expansion coefficient, in which it for the d and p characters can be chosen to be real and pure imaginary, respectively.

If R is a rotation of the cubic point group O_h, then

$$P(R)\,\phi_{\nu\mathbf{k}}(\mathbf{r}) = \phi_{\nu\mathbf{k}}(R^{-1}\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n} \sum_{\alpha} \exp(i\mathbf{k}\mathbf{R}_n)\, B_{\nu\mathbf{k}\alpha}\, \phi_\alpha(R^{-1}\mathbf{r}-\mathbf{R}_n), \tag{2}$$

Introducing the lattice vector $\mathbf{R}_m = R\mathbf{R}_n$, we get $\phi_\alpha(R^{-1}\mathbf{r}-\mathbf{R}_n) = P(R)\,\phi_\alpha(\mathbf{r}')$ in which $\mathbf{r}' = \mathbf{r}-\mathbf{R}_m$. As is well known, using the representation matrix $\Gamma(R)$ of O_h, we obtain

$$P(R)\,\phi_\alpha(\mathbf{r}') = \sum_{\beta} \Gamma(R)_{\beta\alpha}\, \phi_\beta(\mathbf{r}') \tag{3}$$

Note that $\Gamma(R)$ can be reduced to the three irreducible representations for which the

cubic basis functions are (x, y, z), (xy, yz, zx) and $(x^2-y^2, (3z^2-r^2)/\sqrt{3})$. The matrix corresponding to each irreducible representation can be found easily by (3) and is also tabulated in the text of the group theory [10]. On the other hand, on a basis of the Bloch theorem, we get $\phi_{\nu k}(R^{-1}r) = \exp(ik\cdot R^{-1}r)\, u_{\nu k}(R^{-1}r) = \exp(iRk\cdot r)\, u_{\nu k}(R^{-1}r)$ which is a Bloch function $\phi_{\nu, Rk}(r)$ with wave vector Rk. The expansion form for the $\phi_{\nu, Rk}(r)$ similar to (1) can be also written. Thus, we can obtain the relation

$$B_{\nu, Rk, \beta} = \sum_{\alpha} \Gamma(R)_{\beta\alpha}\ B_{\nu k\alpha}. \tag{4}$$

The matrix element $M(\nu' k' : \nu k)$ appearing in $J(R_n)$ is given by

$$M(\nu' k' : \nu k) = \sum_{\alpha} \sum_{\beta}' B_{\nu' k'\beta}\ B_{\nu' k'\alpha}\ B_{\nu k\alpha}\ B_{\nu k\beta}, \tag{5}$$

where α and β are the $5dt_{2g}$ and $5de_g$ states because the intra-atomic d–f Coulomb exchange interaction is assumed in $J(R_n)$. By uses of (4) and the orthogonarity of the matrix $\Gamma(R)$ in which only the irreducible representations for the basis functions with t_{2g} and e_g symmetries are used, we can easily get the symmetry of the matrix element

$$M(\nu', Rk' : \nu, Rk) = M(\nu' k' : \nu k). \tag{6}$$

3. Numerical calculation method of $\chi(Q)$

The RKKY interaction $J(R_n)$ [11] is given by

$$J(R_n) = \frac{2I^2}{N^2} \sum_{\nu}\sum_{\nu'} \sum_{k}\sum_{k'} M(\nu' k' : \nu k)\, \frac{f_{\nu k}(1-f_{\nu' k'})}{E_{\nu' k'} - E_{\nu k}} \exp[i(k-k')R_n], \tag{7}$$

where I is the intra-atomic d-f Coulomb exchange integral, $E_{\nu k}$ the band energy, $f_{\nu k}$ the Fermi distribution function for T= 0K, and $M(\nu' k' : \nu k)$ is the matrix element given by (5). The susceptibility $\chi(\mathbf{Q})$ is defined as the Fourier transform of $J(R_n)$, and is given by

$$\chi(\mathbf{Q}) = \frac{2I^2}{N} \sum_{\nu}\sum_{\nu'} \sum_{k} M(\nu', k+\mathbf{Q}+\mathbf{K} : \nu k)\, \frac{f_{\nu k}(1-f_{\nu', k+Q+K})}{E_{\nu', k+Q+K} - E_{\nu k}}, \tag{8}$$

where the reciprocal lattice vector K is chosen so that the vector k+Q+K can be in the first Brillouin zone (referred to as B. Z below). Because $E_{\nu k}$ and $M(\nu' k' : \nu k)$ calculated in the tight binding model are used in (8), the k integrations over the B. Z must be performed numerically.

As well known, $E_{\nu k}$ has the symmetry of $E_{\nu, Rk} = E_{\nu k}$, in which R is a rotation of O_h. $M(\nu' k' : \nu k)$ has also the symmetry of $M(\nu', Rk' : \nu, Rk) = M(\nu' k' : \nu K)$ as mentioned in § 2. Therefore, from these symmetries, the k integrations over the B. Z can be carried out over one basic section of the B. Z containing only (1/48) of the volume of the B.Z. However, because the shape of the basic section is the intractable pentahedron, we integrate over the more tractable tetrahedron, in which k vector is limited within $0 \leqq k_z \leqq k_y \leqq k_x \leqq 2\pi/a$ and a is the next nearest neighbor distance in the f.c.c. lattice. This tetrahedron can be constructed from the two basic sections mentined above, in which one section is translated by the appropriate reciprocal lattice vector from the B.Z, and therefore its volume is 1/24 of B. Z. Thus, we get

$$\chi(\mathbf{Q}) = \frac{1}{2}\ \frac{2I^2}{N} \sum_{R}\sum_{\nu}\sum_{\nu'} \sum_{k}' M(\nu', k+R\mathbf{Q}+\mathbf{K} : \nu k)\, \frac{f_{\nu k}(1-f_{\nu', k+RQ+K})}{E_{\nu', k+RQ+K} - E_{\nu k}}, \tag{9}$$

where R takes all rotations in O_h and the factor 1/2 is necessary because the volume of tetrahedron is twice of the basic section. The numerical integrations with respect to

k will be carried out by the Rath-Freeman method [12], in which the above mentined tetrahedron is divided into a large number of small tetrahedrons and the band energy is approximated by the linear interpolated formula in each small tetrahedron. The matrix element is replaced by its value at the center of gravity of the small tetrahedron. Furthermore, when the vector k+RQ+K in (9) is outside the original tetrahedron, the matrix element can be calculated using $B_{\nu k\alpha}$ in its tetrahedron from (4).

4. Numerical results and discussions

The band structure used in the numerical calculation of $\chi(\mathbf{Q})$ is shown in fig.1. This is calculated in the tight binding model [8–9], in which the two center integrals are determined so as to fit the APW band calculation of the semimetallic Lap[7]. However, their values are modified a little so that its band structure can denotes the semiconductor with the almost zero band gap. For the details of the band structure, see the references [1, 6–7]. The Fermi energy is chosen to be $E_F = 0.2645$ Ryd, and then the Fermi level stands between the third and the fourth bands.

Let us denote the susceptibility due to the scattering from the ν–th band to the ν'–th band by $\chi_{\nu\nu'}(\mathbf{Q})$. $\chi_{\nu\nu'}(\mathbf{Q})$ is calculated numerically by means of the method mentioned

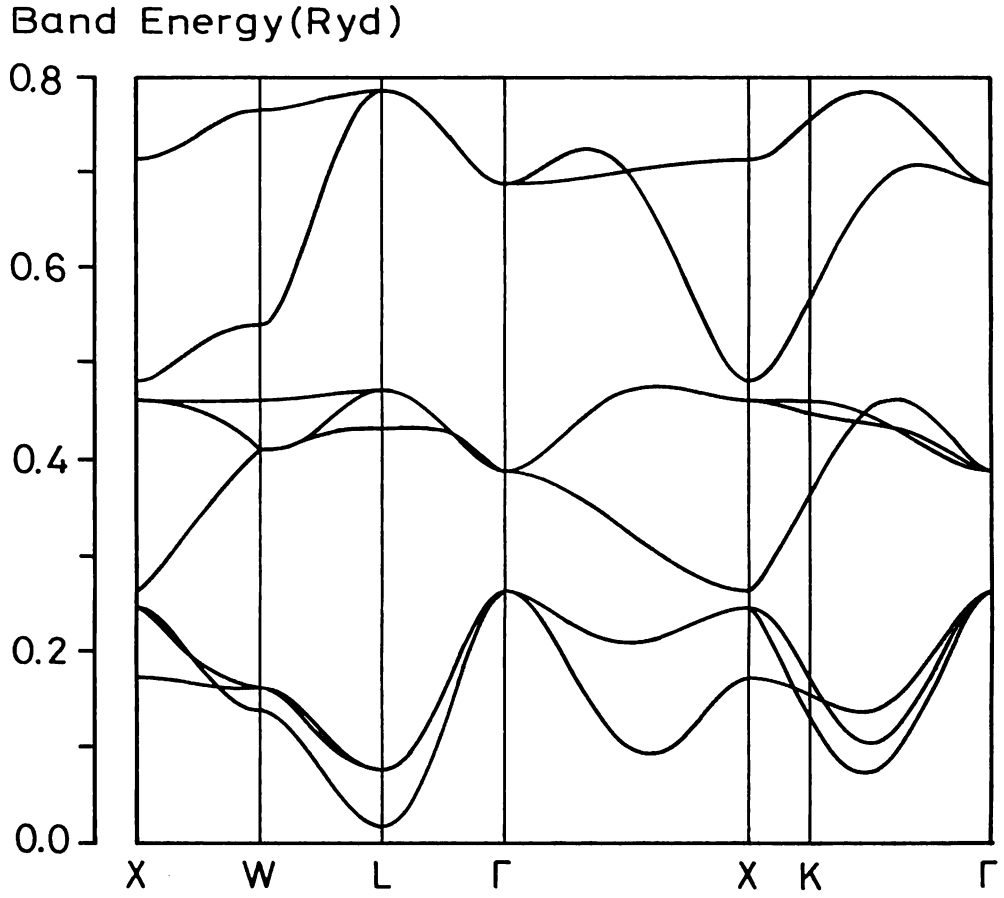

Fig. 1. The band structure due to the tight binding model is shown for the semiconducting material. The values of two center integrals measured in unit of Rydberg are as follows : $p_0=0.232$, $(pp\sigma)=0.015$, $(pp\pi)=-0.0035$, $d_1=0.3933$, $d_2=0.6198$, $(dd\sigma)=-0.02059$, $(dd\pi)=0.02034$, $(dd\delta)=-0.004969$, $(pd\sigma)=0.1188$, $(pd\pi)=-0.04896$.

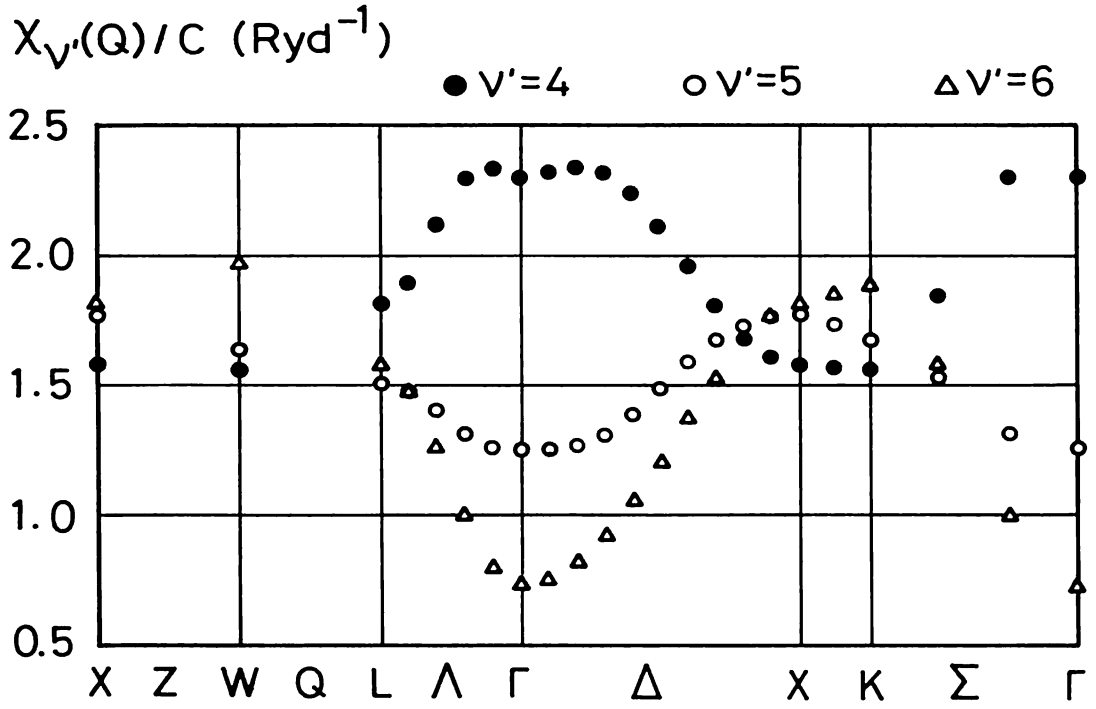

Fig. 2. The susceptibilities $\chi_{\nu'}(\mathbf{Q})/C$ obtained summing the contributions from the all valence bands are shown for $\nu'=4,5$ and 6, and they are measured in unit of Rydberg^{-1}. Black, open circles and triangles denote the $\chi_4(\mathbf{Q})/C$, $\chi_5(\mathbf{Q})/C$ and $\chi_6(\mathbf{Q})/C$, respectively.

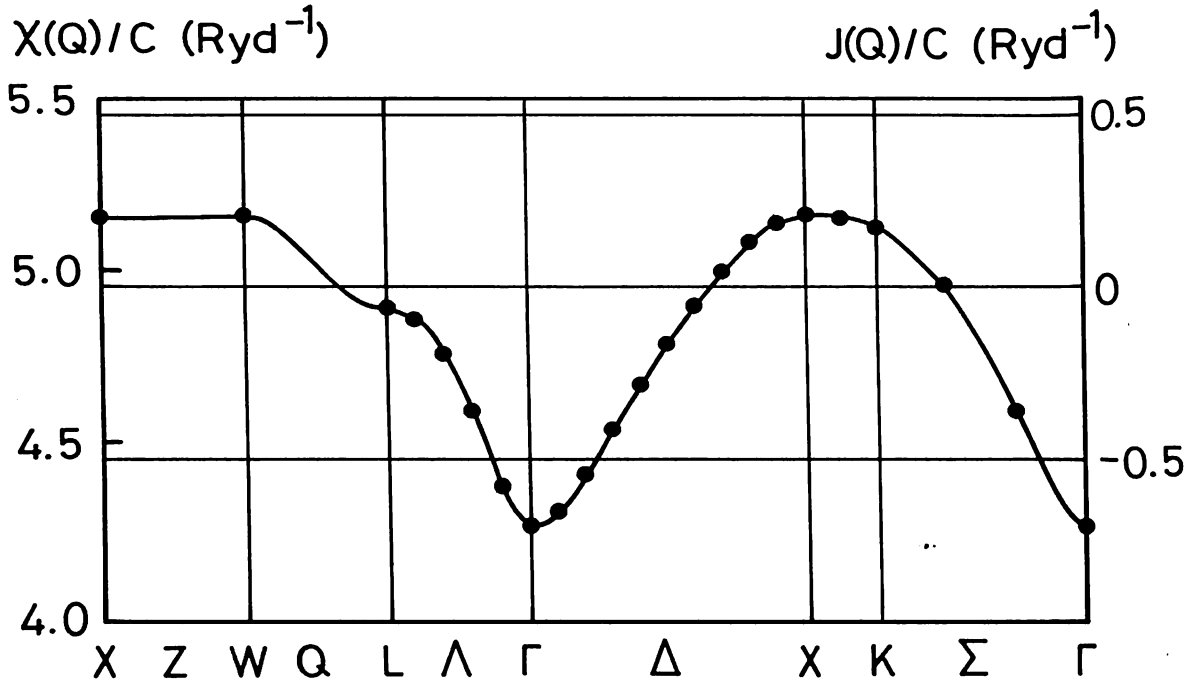

Fig. 3. The total susceptibility $\chi(\mathbf{Q})/C$ measured in unit of Rydberg^{-1} is shown. Black circles denote the numerical datas of $\chi(\mathbf{Q})/C$ calculated numerically. The solid curve is the susceptibility calculated from the Fourier interpolated formula using J_n in the case of d=6.

in §3 for $1 \leqq \nu \leqq 3$ and $4 \leqq \nu' \leqq 6$. $\chi_{\nu\nu'}(\mathbf{Q})$ for $\nu' \geqq 7$ are neglected because the band structure shown in fig. 1 is not fitted to those due to the APW method for LaP for $\nu' \geqq 7$. They are calculated for the 21 $\mathbf{Q}$-vectors in B.Z, which are on the Δ-, the Λ-, and the Σ-axes, and on the W point. Let us denote the contribution due to the scattering from the valence bands to ν'-band by $\chi_{\nu'}(\mathbf{Q})$, that is, $\chi_{\nu'}(\mathbf{Q}) = \sum_{\nu=1}^{3} \chi_{\nu\nu'}(\mathbf{Q})$. $\chi_{\nu'}(\mathbf{Q})$ for $\nu' = 4, 5$ and 6 are shown in fig. 2, in which the normalization constant C is given by $C = 2I^2/Na^3$ because the band energy and the wave vector in (9) are measured in unit of Rydberg and $2\pi/a$, respectively. As easily seen in fig. 2, $\chi_4(\mathbf{Q})$ has the maximum at the Γ-point giving the ferromagnetic ordering. This is contradictory to the previous result in ref. [1] due to the simplified band structure. The reason can not be understood now. Perhaps, it seems that it is due to the complicated effect of the matrix element [14]. $\chi_5(\mathbf{Q})$ and $\chi_6(\mathbf{Q})$ have the almost similar dispersions although that of $\chi_6(\mathbf{Q})$ is larger. Furthermore, they have the maximums at the X and the W points, respectively, stabilizing the antiferromagnetic states. Thus, the fact that $\chi_5(\mathbf{Q})$ and $\chi_6(\mathbf{Q})$ also have the large dispersion means that we can not ignore the scatterings to the higher conduction bands while the scatterings to the conduction band immediately above the Fermi level are of course important. These scatterings to the higher conduction bands seems to be particularly important when the matrix element effect is taken into account. This can be checked by calculating $\chi_{\nu'}(\mathbf{Q})$ in the constant matrix element case [14], in which the wave vector dependence of the matrix element is ignored. Note that for the same reason the scatterings from the valence bands sufficiently below the Fermi level are also important.

The total susceptibility $\chi(\mathbf{Q})$ given by $\sum_{\nu'=4}^{6} \chi_{\nu'}(\mathbf{Q})$ is indicated in fig. 3. Strangely, this total $\chi(\mathbf{Q})$ has the very similar dispersion to the result given in ref. [1]. Fig. 3 gives the antiferromagnetic orderings as the most stable states, because $\chi(\mathbf{Q})$ have the maximum with almost equal amplitude on the Z-axis. However, at this stage, we can not distinctly say about the spin ordering. The RKKY interactions J_n can be determined using the all numerical datas of $\chi(\mathbf{Q})$ by means of the least squares method, in which the Fourier transform is used as the interpolated formula. J_n are considered to be the fitting parameter. When we use the parameters up to J_d, trend of convergence of J_n with increasing of d is shown in table 1. J_n does not converge with increasing of d. They show rather the oscillatory behaviors and for larger n this characteristics is striking. However, for $5 \leqq d \leqq 10$, the numerical datas of $\chi(\mathbf{Q})$ can be very well fitted by uses of J_n thus determined as easily seen in fig. 3. For $d \leqq 4$, agreement between both cases is not so good. For $d \geqq 11$, clearly the physically meaningless solution is obtained, which means that independent more numerical datas of $\chi(\mathbf{Q})$ are necessary for this case.

Fortunately, J_0, which is a selfenergy, has almost the constant value of $J_0/C = 4.95$ Ryd^{-1}. Therefore, we can get $J(\mathbf{Q})$ by subtracting this J_0 from $\chi(\mathbf{Q})$. The scale for the $J(\mathbf{Q})$ is also shown in fig. 3 on the right hand side. But, this J_0 may be too large because it is predicted that its $J(\mathbf{Q})$ does not satisfy the sum rule $\sum_{\mathbf{Q}} J(\mathbf{Q}) = 0$.

The normalization constant C becomes to $C = I^2/2$ because of $Na^3 = 4$ in the f.c.c lattice. From the atomic spectra of Gd, the intra-atomic d-f Coulomb exchange integral is obtained to be $I = 1.46 \times 10^3$ K [15–17]. Therefore, we get $C = 1.066 \times 10^6$ K^2. Using $J(\mathbf{Q})$ in fig. 3 and this value of C, the comparable order of magnitude with experiments [13] for the paramagnetic Curie and the Neel temperatures can be obtained. For example, $\theta_p = -49$K and $T_N = 15$K.

The calculation performed here is contradictory to the experimental fact for GdN that

Table 1. Trend of convergence of J_n due to the least square method. Values of J_0/C and $J_n/C \times 10^3 (Ryd^{-1})$ $(n \geqq 1)$ are listed. d means that the fitting parameters up to J_d are used.

d	J_0	J_1	J_2	J_3	J_4	J_5	J_6	J_7	J_8	J_9	J_{10}	J_{11}
2	4.948	−51.8	0.63									
3	4.939	−47.8	1.55	−3.09								
4	4.953	−48.7	2.69	−2.24	−3.82							
5	4.947	−47.0	4.25	−2.28	−3.56	−1.76						
6	4.946	−47.0	4.54	−2.23	−3.41	−1.80	−0.377					
7	4.947	−47.3	3.98	−1.72	−3.27	−1.49	−0.205	−0.412				
8	4.945	−47.0	4.10	−1.82	−3.34	−1.74	−0.178	−0.363	0.717			
9	4.954	−47.4	3.60	−2.38	−3.38	−1.03	−0.138	0.016	−0.756	−1.367		
10	4.948	−47.3	3.63	−1.55	−3.34	−1.30	−0.125	−0.383	0.364	−0.371	−0.379	
11	12.016	−636.	−1174	−1.54	−3.34	588.	−0.125	−0.384	−1178	−589.4	−0.379	295.

the energies for the ferromagnetic and the antiferromagnetic states are close. As the recent experiment [18] shows, GdN is the semimetal with the small amount of free carriers. It is expected that existence of this free carrier strengthens the ferromagnetic state [1]. The study of this carrier effect will be reported in a separate paper. $\chi(\mathbf{Q})$ for other pnictides, which are also the semimetal with about 0.1 free carriers per Gd [7,19], are reported in a separate paper, too.

5. Conclusion

So far, we have considered the susceptibility using the band energy and the matrix element due to the tight binding model and its analysis for the magnetic semiconductor with a almost zero band gap. The followings are clarified :

(1) The scatterings from the valence bands to the sufficiently higher conduction bands and from the sufficiently deeper valence bands to the conduction band, both are important.

(2) As a whole, the present calculation is accidently in agreement with the previous result due to the simplified band model. But, in detail, both are not in agreement because of the complicated matrix element effect.

(3) When $\mathbf{Q}$ vectors are chosen appropriately, using abot twenty numerical datas of the susceptibility $\chi(\mathbf{Q})$ the RKKY interactions and therefore $J(\mathbf{Q})$ can be determined very well by means of the least squares method.

References

[1] A. Narita and T. Kasuya, J. Mag. Mag. Mater., **52** (1985) 373.

[2] A. Narita and T. Kasuya, in : Extended Abstracts for US-Japan Seminar, Sendai (1977) p. 93.

[3] A. Narita, J. Phys. **C19** (1986) 4797.

[4] A. Narita, Res. Rep. Akita Nat. Colle. Tech., **21** (1986) 47.

[5] T. Kasuya, IBM J. Res. Dev. **14** (1970) 214.

[6] A. Hasegawa and A. Yanase, J. Phys. Soc. Japan **42** (1977) 492.

[7] A. Hasegawa, J. Phys. **C13** (1980) 6147.

[8] J. C. Slater and G. F. Koster, Phys. Rev. **94** (1954) 1498.

[9] A. Nussbaum, in : Solid State Physics ed. Seitz and Turnbull (New York, Academic

Press, 1966) Vol. 18, pp. 165—272.
[10] J. F. Cornwell, in : Group Theory and Electronic Energy Bands in Solids (North-Hollamd Pub. Compa., 1969) Appendix 1.
[11] T. Kasuya, in : Magnetism ed. G. T. Rado and H. Suhl (New York, Academic Press, 1966) Vol. IIB, pp. 215—94.
[12] J. Rath and A. J. Freeman, Phys. Rev. **B11** (1975) 2109.
[13] F. Hulliger, in : Handbook on the Physics and Chemistry of Rare Earths ed. Gschneider and Eyring (North-Holland, 1979) Vol. 4, pp. 153—236.
[14] A. Narita and T. Kasuya, J. Mag. Mag. Mater., **43** (1984) 21—42.
[15] B. G. Wybourne, in : Spectroscopic Properties of Rare Earths (John Wiley and Sons, Inc., 1965)
[16] S. Feneuille and N. Pelletier-Allard, Physica **40** (1968) 347.
[17] B. M. Angelov, J. Phys. **C11** (1978) L713.
[18] P. Wachter and E. Kaldis, Solid State Commun. **34** (1980) 241.
[19] P. Wacter, E. Kaldis and R. Hauger, Phys. Rev. Lett., **40** (1978) 1404.