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The pressure effect on the enhanced itinerant paramagnetism of Ni₃Al and TiCo compounds

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Abstract. The pressure effect on the magnetic susceptibility of Ni₃Al and TiCo compounds is studied in the temperature range 20–293 K. The obtained magnetovolume effect values $d \ln \chi / d \ln V$ and results of detailed theoretical calculations of density of states at the Fermi level as a function of the lattice constant were used to evaluate volume derivatives of the electron–electron interaction parameter J : $d \ln J / d \ln V = -0.9 \pm 0.15$ (Ni₃Al) and -0.95 ± 0.15 (TiCo). These results are compared with theoretical estimates of $d \ln J / d \ln V$ from *ab initio* LMTO band structure calculations.

1. Introduction

Electron–electron interactions play a fundamental role in the properties of metallic systems and account for the current interest in revealing the microscopic nature of the interactions and their behaviour for particular types of metal and compound. These interactions manifest themselves in magnetic properties through the enhancement of the Pauli spin susceptibility χ_P by the Stoner factor S :

$$\chi = S\chi_P = \frac{\mu_B^2 N(E_F)}{1 - JN(E_F)} \quad (1)$$

where $\chi_P = \mu_B N(E_F)$, $N(E_F) \equiv N$ is the density of states at the Fermi level E_F , J is the interaction parameter. In the case where $JN \cong 1$ (for strong itinerant paramagnets or weak ferromagnets at $T > T_c$), the predominance of contribution (1) makes the magnetic susceptibility of such systems an efficient tool for the study of the interaction parameter and, in particular, its dependence on the atomic volume.

With increasing Ni content, a transition from enhanced paramagnetism to weak ferromagnetism occurs in the system of Ni₃Al alloys, the stoichiometric Ni₃Al compound being an itinerant ferromagnet with $T_c \cong 43$ K. Their magnetic properties and magneto-volume effects (magnetostriction, pressure dependences of the Curie temperature and magnetization) were studied thoroughly in [1, 2]. Some magnetic properties of the TiCo compound were determined in connection with the study of the ferromagnetic ternary compounds Fe_xCo_{1-x}Ti [3] and CoTi_{1-x}Al_x [4]. They indicate the TiCo compound to be an enhanced paramagnet (with $S \cong 10$). Its magnetostriction at $T = 4.2$ K was measured in [5].

In the present work, the available experimental data on the low-temperature magnetovolume effect in Ni_3Al and TiCo compounds are supplemented by direct measurements of the pressure effect on their magnetic susceptibility over a wide range of temperatures. In order to extract the change in interaction parameters with pressure from the observed magnetovolume effects, band structures and densities of states $N(E)$ of Ni_3Al and TiCo were calculated as functions of the atomic volume. Using these results, volume derivatives of the electron-electron interaction parameter $d \ln J / d \ln V$ have been evaluated and compared with similar values, obtained for other strong itinerant paramagnets. Corresponding theoretical estimates were carried out in the frameworks of the local spin density approximation (LSDA) and the Hubbard model.

2. Experimental technique and results

The measurements of the magnetic susceptibility under pressures up to 4 kbar for temperatures 20–300 K were carried out by two methods: the Faraday method with the pendulum magnetometer placed directly into the high-pressure chamber [6] and the levitation method [7]. The relative error did not exceed 0.05% in either case. The pressure was produced by gaseous helium using a membrane compressor [6]. The polycrystalline samples of near-stoichiometric $\text{Ni}_{74.8}\text{Al}_{25.2}$ and $\text{Ni}_{75.5}\text{Al}_{24.5}$ compounds and stoichiometric TiCo compound were prepared from ingots, used earlier in [1, 2, 4]. The pressure dependences of their susceptibility are linear (figures 1, 2), yielding values for $d \ln \chi / dP$. The corresponding volume derivatives, $d \ln \chi / d \ln V$, are listed in table 1 (the bulk modulus values $B_{\text{Ni}_3\text{Al}} = 1.7$ Mbar [8, 9] and $B_{\text{TiCo}} = 2.0$ Mbar [10] were used for evaluation from $d \ln \chi / dP$).

As long as the enhanced spin paramagnetism (1) is the main contribution to the magnetic susceptibility of Ni_3Al and TiCo in the considered temperature range, the value of the magnetovolume effect $d \ln \chi / d \ln V$ is given by:

$$\begin{aligned} d \ln \chi / d \ln V &= \frac{d \ln N}{d \ln V} + \frac{JN}{(1 - JN)} \left(\frac{d \ln N}{d \ln V} + \frac{d \ln J}{d \ln V} \right) \\ &= \frac{d \ln N}{d \ln V} + \chi \mu_B^{-2} J \left(\frac{d \ln N}{d \ln V} + \frac{d \ln J}{d \ln V} \right). \end{aligned} \quad (2)$$

As follows from (2), the value of $d \ln \chi / d \ln V$ for different temperatures and/or compositions of alloys can be approximated by a linear function of the magnetic susceptibility, in the case where the parameters $d \ln N / d \ln V$, $d \ln J / d \ln V$ and J depend weakly on temperature and composition. In figure 3 the dependence of the experimental $d \ln \chi / d \ln V$ values on the susceptibility is presented for the $\text{Ni}_{74.8}\text{Al}_{25.2}$ alloy. In accordance with (2), this dependence is linear and can be described by the following relations between the parameters:

$$J(d \ln N / d \ln V + d \ln J / d \ln V) = 15.3 \pm 1.5 \text{ mRyd spin atom Ni} \quad (3)$$

$$d \ln N / d \ln V \cong 1. \quad (4)$$

The data for the $\text{Ni}_{75.5}\text{Al}_{24.5}$ alloy at $T = 77.8$ K (see table 1) follow the same relationship, but are not displayed in figure 3 due to the different scales. This confirms the weak response of the parameters (3) and (4) to temperature and to small deviations from stoichiometry.

Setting $J = 75 \pm 10$ mRyd spin atom Ni, in accord with the calculations [11] and experimental estimates [1], we can obtain from (3)

$$d \ln N / d \ln V + d \ln J / d \ln V = 0.20 \pm 0.05 \quad (5)$$

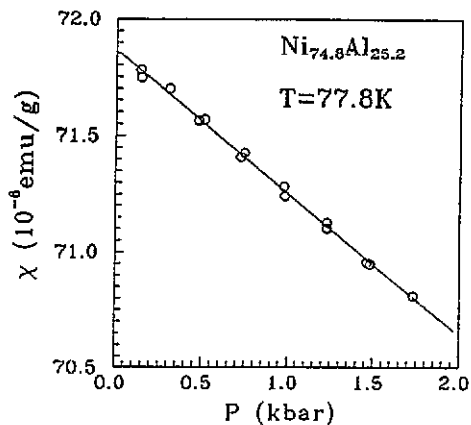


Figure 1. Pressure dependence of the magnetic susceptibility in $Ni_{74.8}Al_{25.2}$ at 77.8 K.

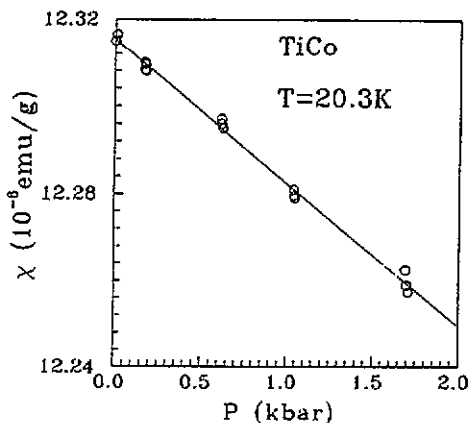


Figure 2. Pressure dependence of the magnetic susceptibility of $TiCo$ at 20.3 K.

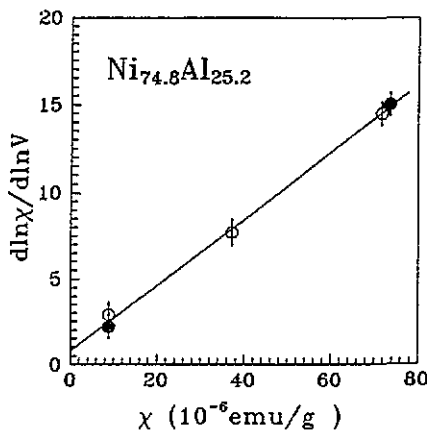


Figure 3. The value of $d \ln \chi / d \ln V$ as a function of the magnetic susceptibility for the compound $Ni_{74.8}Al_{25.2}$ (the full circles represent the data obtained by the levitation method).

This value follows closely the result of magnetovolume experiments [1] for the ferromagnetic phase.

As far as the magnetovolume data for $TiCo$ compound are concerned, it seems unreasonable to present them in the manner of figure 3 due to a small change of magnetic susceptibility in the considered temperature range. In such a situation, the low-temperature value of $d \ln \chi / d \ln V$ is more suitable for the analysis. It should be noted that our value of $d \ln \chi / d \ln V$ at $T = 20.3$ K is about half the value that resulted from the magnetostriction data at $T = 4.2$ K [5]. The origin of this discrepancy is still unclear.

3. Band structure calculations and analysis

The obtained crude estimate of the band contribution (4) is insufficient for a correct separation of terms in (5). In this connection, *ab initio* calculations of band structures have been carried out for the Ni_3Al and $TiCo$ compounds, having the Cu_3Au and $CsCl$

Table 1. Experimental values of the magnetic susceptibility χ , its volume derivative $d \ln \chi / d \ln V$ and calculated values of the density of states at the Fermi level $N(E_F)$ and its volume derivative $d \ln N(E_F) / d \ln V$ for Ni_3Al and $TiCo$.

Compound	T (K)	χ (10^{-6} emu g^{-1})	$d \ln \chi / d \ln V$	$N(E_F)$ (cell Ryd) $^{-1}$	$d \ln N(E_F) / d \ln V^a$
Ni_3Al	77.8	71.8	14.5 ± 0.7	93.16	1.04
		73.5^b	15.0 ± 0.7^b		
		$(245)^c$	$(45 \pm 2)^c$		
	111.0	37.2	7.7 ± 0.8	92.91	1.08
293.0	8.9	2.9 ± 0.8	88.61	1.16	
			2.2 ± 0.7^b		
$TiCo$	20.3	12.3	5.4 ± 0.4^b	40.67	1.60
	77.8	11.5	5.3 ± 0.4^b	40.12	1.54
	290.0	8.32	4.4 ± 0.4	39.08	1.28

^aThe error in the calculation is accepted to be ± 0.1 .

^bData by the levitation method.

^cFor the compound $Ni_{75.5}Al_{24.5}$.

crystal structures, respectively. The relativistic version (including spin-orbit coupling) of the LMTO method was employed in the atomic sphere approximation [12, 13]. Individual atomic radii of the components were chosen following the general rule, proposed in [14]. The minima of the total energy are found at $a = 3.55 \text{ \AA}$ (Ni_3Al) and $a = 3.02 \text{ \AA}$ ($TiCo$), close to the experimental lattice parameter values.

In order to extract the change of J with pressure from the observed magnetovolume effect, the $d \ln N(E_F) / d \ln V$ values in (2) have to be known. With this purpose, the electronic structures were calculated on a uniform mesh of 455 k points in the irreducible wedge of the cubic Brillouin zone for a number of lattice constant values near the experimental ones. The detailed density of state curves $N(E)$ were elaborated for Ni_3Al and $TiCo$ using the tetrahedron integration scheme on a very fine energy mesh (0.01 mRyd). The sections of the $N(E)$ curves at the corresponding Fermi energies are displayed in figures 4 and 5 and found to be close to the obtained earlier dependences for Ni_3Al [11, 15, 16] and $TiCo$ [10, 17].

For finite temperatures the effect of 'smearing' through the Fermi-Dirac distribution function $f(E, \mu, T)$ has been taken into account:

$$N(\mu, T) = \int N(E) [-\partial f(E, \mu, T) / \partial E] dE. \quad (6)$$

The values of the chemical potential μ were determined from the condition that the number of electrons, Q , per cell is constant:

$$Q = \int N(E) f(E, \mu, T) dE. \quad (7)$$

The evaluated $N(E_F)$ and $d \ln N(E_F) / d \ln V$ values are presented in table 1 and figures 6 and 7. Our calculated $N(E_F)$ values are consistent with previously obtained results [10, 15-17].

For compositions and temperature complying with the experiment, $d \ln N(E_F) / d \ln V$ derivatives vary slightly, and can be represented by their mean values $d \ln N(E_F) / d \ln V = 1.1$ and 1.3 for Ni_3Al and $TiCo$, respectively. As can be seen in figures 6 and 7, it does not hold true either for lower temperatures, or for large deviations from stoichiometry.

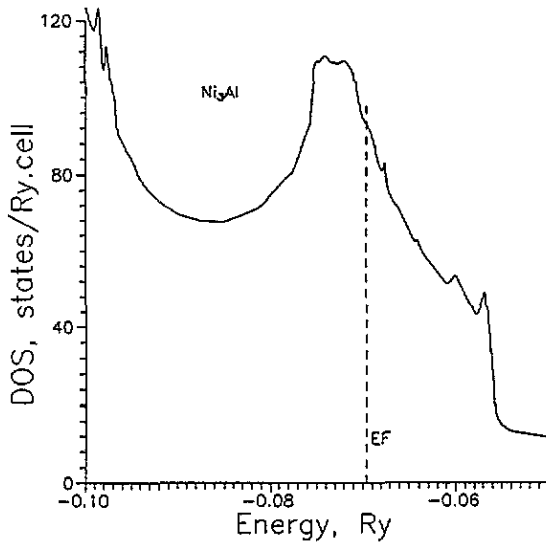


Figure 4. The density of states of Ni_3Al in the vicinity of the Fermi energy.

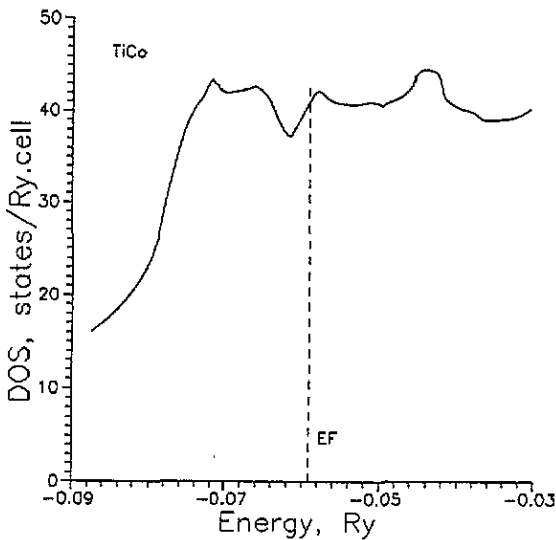


Figure 5. The density of states of $TiCo$ in the vicinity of the Fermi energy.

Moreover, the latter value is related to $Q = 13.05$ in figure 7. For such a filling of the $TiCo$ band the calculated $\chi(T)$ is consistent with the experimental one, and the corresponding energy shift $\Delta E_F = 1$ mRyd falls within the accuracy of the calculations. These derivatives definitely deviate from the value $\frac{5}{3}$, corresponding to the uniform widening of the d band under pressure [18]. It seems rather to be related to the non-uniform deformation of the $N(E)$ fine structure near the Fermi level, than to the electron transfer between sp and d bands [19].

Substituting $d \ln N(E_F)/d \ln V$ derivatives in (2) together with the experimental values of χ and $d \ln \chi/d \ln V$ from table 1, and the accepted estimates of J (in $TiCo$ the calculated value is $J = 38$ mRyd spin cell), volume derivatives of the electron-electron interaction

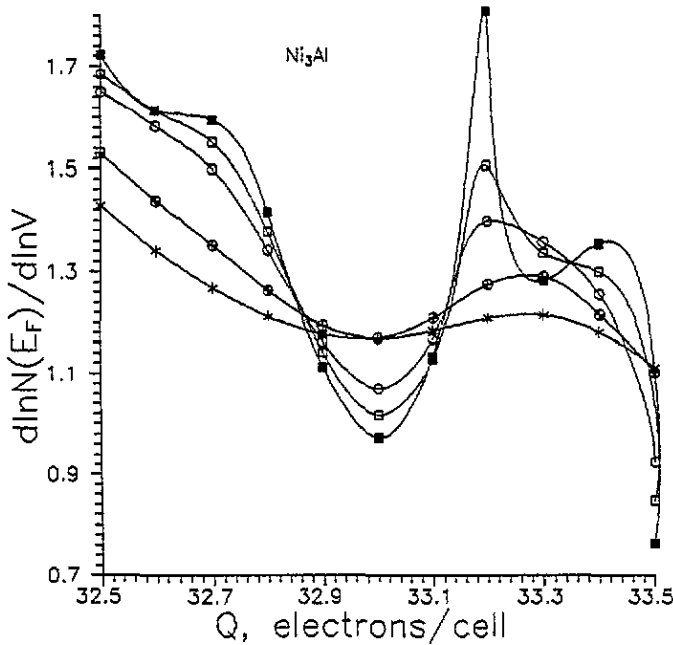


Figure 6. The logarithmic derivative of the density of states of Ni_3Al at the Fermi level with respect to the atomic volume, versus band filling Q . Temperatures: ■, 40 K; □, 78 K; ○, 100 K; ⊕, 200 K; *, 300 K.

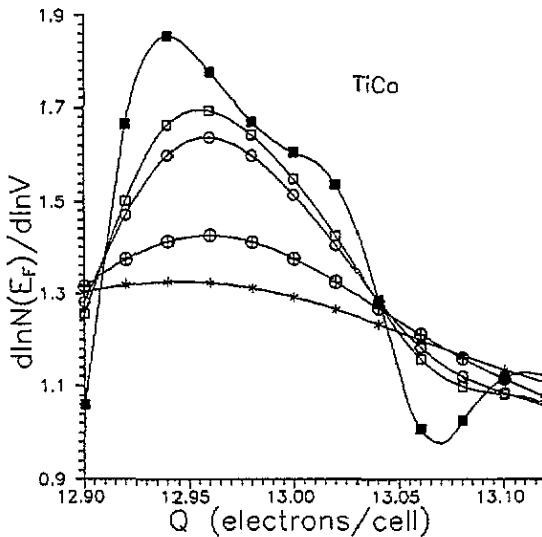


Figure 7. The logarithmic derivative of the density of states of TiCo at the Fermi level with respect to the atomic volume, versus band filling Q . Temperatures: ■, 20 K; □, 78 K; ○, 100 K; ⊕, 200 K; *, 300 K.

parameter $d \ln J / d \ln V$ were evaluated in the considered temperature region: -0.90 ± 0.15 and -0.95 ± 0.15 for Ni_3Al and TiCo , respectively. The result follows closely the analysis of the magnetovolume data for Ni_3Al in the ferromagnetic state [1], provided the calculated value of $d \ln N(E_F) / d \ln V$ is used.

4. Discussion

Only one-particle thermal excitations were taken into account in this evaluation. For Ni₃Al, a substitution of calculated values $N(E_F, T)$ into (1) gives us about half of the experimental $\chi(T)$ dependence in the range 80–300 K. The remaining part can be attributed to spin fluctuations. In the simplified form this mechanism can be taken into account by means of an additional term in the interaction parameter J : $J(T) \simeq J(0) + \beta T$ [20], where β is a constant, determined by the electronic spectrum features. Accordingly, the additional term appears in (2):

$$\chi \mu_B^{-2} J [\beta T / J] \left(\frac{d \ln N}{d \ln V} + \frac{d \ln \beta}{d \ln V} \right)$$

which is $\beta T / J$ times the main (second) term. The factor $\beta T / J$ can be estimated from the $\chi(T)$ dependence, having Curie–Weiss behaviour in Ni₃Al. Even if the whole dependence is related to spin fluctuations, $\beta T / J$ does not exceed 0.05 at $T \cong 100$ K. Therefore, the influence of this mechanism on the magnetovolume effect (but not on the $\chi(T)$ itself!) can be neglected. This conclusion is valid for any other mechanism of a temperature dependence of the susceptibility, provided that the additional temperature-dependent contributions to the quantity JN are relatively small.

The evaluated derivatives are close to the corresponding values, obtained for strong itinerant paramagnets—vanadium [7], palladium alloys [21], (Fe–Co)Si [22] and U(Fe–Mn–Co)₂ alloys [23], for which the $d \ln J / d \ln V$ values fall in the region $-(0.7-1.3)$. These values of the derivative differ considerably from the results of the LSDA calculations for d metals and their compounds: 0 to -0.2 [24]. Only one result is totally different from other calculated values: $d \ln J / d \ln V = -2.6$ for Ni₃Al [15]. Actually, this result was obtained from the d band splitting for the spin-polarized calculation. Presumably, it is related to a specific feature of the Ni₃Al electronic spectrum as revealed in [16]. Namely, at the equilibrium volume the total energy differences between the paramagnetic and ferromagnetic states are barely detectable. Therefore, the deformation of the spin-polarized subbands has to be taken into account with extreme caution for a quantitative evaluation of $d \ln J / d \ln V$ in Ni₃Al.

Here, we have pushed the precision of the LMTO calculations to its limit by determining $N(E)$ from 455 k points in $\frac{1}{48}$ of the Brillouin zone and obtained $d \ln J / d \ln V = -0.1$ and -0.2 through direct calculation of the exchange integrals (according to [25]) for TiCo and paramagnetic Ni₃Al, respectively. For the spin-polarized band structure of Ni₃Al, a value for the magnetic moment, m , of $0.032 \mu_B / \text{cell}$ was obtained at the calculated lattice parameter. This value is closer to the result in [15] ($0.023 \mu_B$) and to the experimental one ($0.077 \mu_B$ [1]) than to the calculated values at the experimental lattice parameter ($0.44 \mu_B$ [11] and $0.34 \mu_B$ [16]).

Therefore, LSDA calculations employing the exchange–correlation potential of a uniform electron gas are not very well suited for an explanation of the volume dependence of J in d metals. The Hubbard approach, taking into account the energy of the intra-atomic Coulomb repulsion U , is more appropriate for localized d electrons in narrow bands, exhibiting a non-uniform density. For the Hubbard model, the relation between the interaction parameter J and the d band width W appears to be due to the balance between a gain in Coulomb and a loss in band structure energies for the electrons [24]:

$$d \ln J / d \ln V = (d \ln W / d \ln V) f(W / U, Q). \quad (8)$$

Here, the coefficient f depends on the band filling Q , the ratio W / U , and the crystal structure. Therefore, due to correlations, an appreciable volume dependence of J results

from a change of the d band width with pressure. For $U = \infty$, f appears to be unity, and in this case the band width remains the single energy parameter [26]. Therefore $d \ln J/d \ln V \geq -\frac{5}{3}$.

In the context of modern versions of the Hubbard model [24, 27], typical estimates give $d \ln J/d \ln V = -(0.7-1.2)$ for the studied systems. This complies with the experiment and confirms the predominant role of short-range correlations in electron-electron interactions for d metals and their compounds. For these systems further theoretical and experimental investigations of the electron-electron interactions are most interesting, in particular for revealing the functional relationship between the interaction parameters and the electronic spectrum features.

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