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生 年 月 日	
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授与の題目	X-ray diffraction Measurement Below 1K（1K以下のX線回折測定）
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学 位 論 文 要 旨

We have developed the low temperature x-ray diffraction measurement system by a counter detector method for powder samples, by using the ^3He-^4He dilution refrigerator and x-ray diiffractometer. The x-ray beam was reduced approximately 1/12, after passing through 4 walls of Be 2mm thick, 2 Al film 10μm thick and 2 aluminized mylar walls and the lowest temperature was about 0.20K. By using our developed x-ray measurement system at first we have studied the cooperative Jahn-Teller phase transition of $TmVO_4$. And also we have studied the cooperative Jahn-Teller phase transition of $ZnCr_2O_4$ down to 0.20K. This compound undergoes crystallographic phase transition from cubic to tetragonal at the transition temperature T_c=15K. These results suggest that we are able to measure the x-ray diffraction below 1K properly. We studied the orbital ordering materials of PrPtBi and $Ce_{0.75}La_{0.25}B_6$. We measured the full width at half maximum, lattice constant and the intensity of the reflection line. These values gave us useful informations about these compounds.

Many interesting materials show the phase transitions at temperatures below 1K. The crystal structure may be the most essential information to understand the new phase below the transition temperature. For this purpose we have developed the low temperature x-ray diffraction measurement system by a counter detector method for powder samples, by using the ^3He-^4He dilution refrigerator and x-ray diiffractometer. The x-ray beam was reduced approximately 1/100 after passed through 4 walls of Be 2mm thick and 4 aluminized mylar. The lowest temperature of our measurement system was about 0.18K.

We are concerned about the temperature difference between the specimen and the thermometer. To investigate this at first we have studied $TmVO_4$. This compound undergoes cooperative Jahn-Teller phase transition at T_c=2.15K. We have studied the static strain as a function of temperature for (220) reflection. The result of the measurement of static strain shows that the agreement between our experimental result and the previous result measured by A. Segmüler et al and also with the molecular field approximation is rather good. This result suggests that we are able to measure the x-ray diffraction below 1K properly.

Secondly, we have improved our measurement system, by replacing the aluminized mylar film of the radiation shield with 10μm Al film, which was placed between the Outer Vacuum Can (OVC) and the nitrogen bath. With this condition the x-ray beam was reduced approximately 1/12, after passing through the windows of the dilution refrigerator. Then the windows are consisting of 4 walls of Be 2mm thick, 2 Al film 10μm thick and 2 aluminized mylar walls and the lowest temperature was about 0.20K. With this condition, we have studied the cooperative Jahn-Teller phase transition of $ZnCr_2O_4$ down to 0.20K. This compound undergoes crystallographic phase transition from cubic to tetragonal at the transition temperature T_c=15K. Below the transition temperature, whether the c/a<1 or c/a>1 was unknown for this purpose we have studied this compound. Below the transition temperature i.e., $T<T_c$ we have observed that the tetragonal 800 reflection line split into two lines. From our measurement we have got that c/a=0.998 which was less than 1.

We also investigated the temperature difference between the specimen and the mixing chamber by using a carbon resistance of 100Ω. For this purpose we attached a carbon resistance on the sample holder. The experimental results suggest that there is no temperature difference between the specimen and RuO_2 down to 0.5K. Below this temperature the gradient was observed to some extent.

Thirdly, we have studied the orbital ordering materials of PrPtBi and $Ce_{0.75}La_{0.25}B_6$. In these compounds, it was found that the electric orbital took important roll in their low temperature phases.

In the cubic semiconductor compound PrPtBi, the ground state of Pr^{3+} ion is a non-magnetic Γ_3 doublet. To investigate whether the phase transition at 1.35K is antifrro-quadrupolar (AFQ) or ferro-quadrupolar (FQ) type ordering, we have studied this compound by our x-ray measurement. Below the transition temperature we could not observe the splitting of any reflection lines but the full width at half maximum (FWHM) increases with decreasing temperature, which suggests the phase transition at 1.35K is AFQ ordering. We also measured the temperature dependence of the lattice constant d and integrated intensity of the reflection lines. The intensity of the reflection line shows very interesting result. According to the Debye-Waller theorem the intensity increases exponentially with decreasing temperature. The temperature dependence of the integrated intensity for (400) reflection shows that at higher temperatures, say about 30K the temperature dependence of the intensity can be explained by the Debye-Waller factor. At lower temperatures, however, the intensity variation on temperature, is rather complicated. Below about 30K, the intensity starts to decrease till about 10K, then it again increases with decreasing temperature. According to the Debye-Waller theorem, the lattice vibration, that is, the frequency ω, is assumed to be constant expect for $T\cong 0$. At $T\cong 0$, the only zero point motion is taken account. At higher temperatures, the thermal effect is so large that it smeared out the effect due to the change of the force constant in the lattice, which correspond to the change of the ω value. Also for (440) reflection the temperature dependence of the integrated intensity for shows that at higher temperatures say about 50K the temperature dependence of the intensity can be explained by the Debye-Waller factor. Below about 50K, the intensity starts to decrease till about 10K, then it increases up to 2K and again start to decrease with decreasing temperature. The temperature dependence of the integrated intensity for (440) reflection in the low temperature range is different from (400) reflection. The elastic constants $(C_{11}-C_{12})/2$ and C_{44} were measured for PrPtBi compound by Goto et al. It shows that the softening of transverse C_{44} occurs in the low temperature range and the temperature dependence of $(C_{11}-C_{12})/2$ show anomaly at about 2K.

This temperature dependence of the intensity at low temperatures must reflect the change of the lattice properties, such as softening and also the phase transition. This must be the first x-ray measurement, which succeeded to observe the elastic properties

We have investigated the temperature dependence of the lattice constant for the (400) and (440) reflections. The temperature dependence of the lattice constant for (400) reflection shows that at higher temperatures, say about 20K it can be explained by the quantum mechanical equation. At lower temperatures, it increases with decreasing temperature, that is, the negative thermal expansion. Slawomir et. al explain this negative thermal expansion by the Gibbs free energy for Si. They explain that this negative thermal expansion arises due to the negative slope of the vibrational entropy $-S^{vib}T$. They also suggest that this type of thermal expansion should occur for all systems with two atoms per unit cell, provided the acoustical and optical-phonon branches are well separated.

In the cubic semiconductor compound $Ce_{0.75}La_{0.25}B_6$, the ground state of Ce^{3+} ion is a Γ_8 quartet. This specimen contains 4 phases. Phase I is the paramagnetic phase, phase II is the AFQ order state, phase III is the AF (antiferro) magnetic ordered state and the phase IV whose transition temperature lies between 1.4K and 1.7K (or 1.1K and 1.6K) was unknown. To clarify phase IV, we have studied this material. Below the transition temperature 1.7K, we have observed that the FWHM decreases and the intensity of the x-ray peak increases. At 1.5K the peak slightly shifted to the higher angle.

学位論文審査結果の要旨

7 月 31 日に学位論文審査会を開催した。

Shumsun さんはグループで開発した「1K 以下の X 線回折装置」の開発研究に当初から参加し重要な寄与をした。この装置の一応の完成以来，改良を加えながら幾つかの測定を行って来た。

Jahn-Teller 結晶変態を示す $TmVO_4$ の研究では転移温度 2.1K に対してこれまで最低温度 1.7K であった X 線による研究に対して，温度領域を 0.2K まで拡げてほぼ絶対 0 度に近い領域の情報を得ることが出来，この装置の有意義さを示した。又これまで未定であった $ZnCr_4O_4$ の同じく Jahn-Teller 歪による結晶の軸比 c/a の値を決定した。これらの実験を踏まえて現在の磁性のトピックスである電子軌道秩序状態の研究を行った。特に PrPtBi 試料の 1.35K 以下で示す軌道秩序状態に対して X 線を用いた詳細な研究を行いその軌道秩序状態が反強磁性的であることを示した。さらに相転特点で X 線の強度，線巾，格子定数が急激な変化を示すことを見つけた。これらの発見は今後大きく発展することが期待される。

このように新しい発見を多く含み将来の発展も期待出来る内容の論文である。
博士に充分値する論文と判定し Shumsun さんの学力も博士に値するものと判断した。